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PHYSICAL CHEMISTRY OF HIGH POLYMERS PROGRESS REPORT VI

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TECHNICAL REPORT AFML-TR-65-163

SEPTEMBER 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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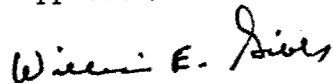
FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the AF Materials Laboratory, Research and Technology Division. Dr. William E. Gibbs was the project engineer.

This report covers work conducted from 1 March 1964 to 1 March 1965.

Manuscript released by the authors May 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

A handwritten signature in dark ink, appearing to read "William E. Gibbs". The signature is written in a cursive, slightly slanted style.

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

The previously reported theoretical consideration of stationary-state conditions in an isothermal polymerization has been extended to cases where the reaction temperature rises linearly throughout polymerization. A solution has been obtained as criteria for the existence of stationary-state conditions in terms of the following inequality: $f[I]k_t/k_d \geq N^2/64$, where f is the efficiency factor (ie., the fraction of radicals produced that initiate growing chains), $[I]$ is the concentration of initiator, k_d is the rate constant for initiator decomposition, k_t is the rate constant for termination, and N is a large number selected so that $1/N$ represents the relative error desired due to deviation from stationary-state conditions. This work indicates that the stationary-state situation prevails in the differential thermal analysis studies on styrene polymerization within the limits of conditions presently used.

Differential thermal analysis studies of the thermodynamics and kinetics of styrene polymerization in solution initiated by AIBN has yielded thermograms which are reasonably consistent and reproducible over the entire temperature span of the reaction. Rate data appear reasonable for temperatures up to 100°C, but above 100°C the rate slows appreciably. A rather detailed examination of the entire system has not yet yielded a solution to the problem.

Raw VPC data has been collected on a model chain transfer system to study the kinetics of cyclopolymerization. Calculations of rate constants from the data have not been completed.

Attempts to synthesize ladder structured polymers have produced stable polyhydrazide materials of extremely low molecular weight ($D.P. \cong 3$). An increase in D.P. could not be achieved due to the poor solubility characteristics of polyhydrazides. Ladder structure polyester syntheses have not been successful due to intramolecular ring formation tendencies. Only dimers and/or gels have been obtained thus far.

The techniques of ultracentrifugation have been improved by the installation of a temperature control system, fabrication of special cells and the invention of new pycnometers. Density gradient techniques are being developed for the study of novel polymer systems. Theoretical investigations have led to derivations of expressions for use in treating sedimentation data at variable centrifugal velocities and flows and for describing sedimentation phenomena in the neighborhood of the meniscus.

Instrument changes have been made on the research apparatus for making light scattering measures. A new thermostatic cell and beam splitting device have been developed. Changes of optical parts for trapping stray light and optical bench design for adapting a laser light source have been made.

Solution properties studies on Phenyl-T ladder polymers have continued and similar studies on PBI have been initiated. Phenyl-T has been fractionated and the $[\eta] = KM^a$ equation in benzene at 25°C has been determined ($K = 1.595 \times 10^{-5}$; $a = 0.909$). Variation of Huggin's constants and second virial coefficients with molecular weight have been determined. The data suggests that Phenyl-T does not behave as a flexible molecule. Theta temperatures for Phenyl-T theta solvents, ethylene dichloride, o-xylene and alpha-chlorotoluene, are being determined. Preliminary results of PBI fractionation and determination of solution properties by viscosity, osmometry and sedimentation are discussed.

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INTRODUCTION

The research described in this report is directed toward the accomplishment of two broad objectives: (a) the discovery and elucidation of novel polymer forming reaction systems and (b) the determination of basic molecular structure-property relationship of new polymer systems. Other reports (Reference 1) refer to earlier work carried out by this laboratory in these areas.

INVESTIGATION OF POLYMER FORMING REACTION SYSTEMS

REACTION KINETICS AND MECHANISMS

The successful synthesis of new, more useful polymeric materials requires an understanding of the basic principles which govern the formation of polymers. For this reason, effort to increase our basic knowledge of reaction mechanisms continues.

1. Stationary State Kinetics

Previously we have discussed (Reference 1) the applicability of the stationary-state assumptions to isothermal polymerization of vinyl monomers initiated by thermal decomposition of free radical initiators. The main purpose of this work was to define criteria for the existence of a stationary-state situation not only for isothermal polymerization, but also for polymerizations conducted as the temperature of the reaction increases linearly throughout the polymerization. The extension of the work to consider this latter case has now been completed. The results reported here are those of particular concern to the determination of kinetic parameters from differential thermal analysis measurements of polymerizing systems.

The criteria for establishment of a stationary-state condition for polymerizations at increasing temperature can be expressed as the inequality:

$$f [I] k_t / k_d \geq N^2 / 64 \quad (1)$$

where: f is the efficiency factor (that is, the fraction of initiator radicals initiating chains); $[I]$ is the molar concentration of initiator; k_d and k_t are, respectively, the rate constants for initiator decomposition and chain termination.

Applying the Arrhenius equation for the temperature dependence of the pertinent rate constants involved in polymerization, it can be shown that:

$$\ln r = \ln (A_p / A_t^{1/2}) + [(E_t / 2 - E_p) / R] 1/T \approx \ln (k_{p,0} / k_{t,0}^{1/2}) + (h_p - 1/2 h_t) t \quad (2)$$

where: $r = k_p / k_t^{1/2}$; A_i and E_i are the frequency factor and the activation energy of a corresponding rate constant k_i (i - is the corresponding general index), $k_{i,0}$ is the initial value of k_i (at $T=T_0$), $h_i = (E_i \dot{T}) / RT_0^2$, and \dot{T} is a constant rate of temperature increase. It is evident from Equation 2, that the plot of $\ln r$ vs. t or $1/T$ must be linear.

Unfortunately, the plot obtained from the experimentally observed DTA curves could be only considered linear if $T \leq T^*$, where $100^\circ\text{C} < T^* < 105^\circ\text{C}$. Beyond this point the deviation from linearity was very significant. Therefore, it was necessary to examine the described polymerization and to select factors possibly responsible for such a discrepancy.

Since the formula applied for the computation of r was derived assuming a stationary state, it was important to prove if such an assumption was justified for $T > T^*$. This question can now be answered by making use of the newly derived stationary state criterion for free radical polymerization at linearly increasing temperatures.

By substituting an appropriate expression for $[I]$ into Equation 1 (Reference AFML TR 64-405) and by assuming $f = 1$, the following formula can be derived:

$$-\log \delta = \log N = \frac{1}{2} \log \left\{ \frac{8 I_0 k_{t,o}}{k_{d,o}} \exp \left[(h_t - h_d) t \right] \right\} - \frac{0.2172 k_{d,o}}{h_d} (e^{h_d t} - 1), \quad (3)$$

where $\delta = \frac{1}{N}$ is the maximum error caused by stationary state assumption.

According to the experimental conditions:

$$\begin{aligned} I_0 &= 5.25 \times 10^{-3} \text{ mol/l}; & \dot{T} &= 1.027 \times 10^{-2} \text{ }^\circ\text{K/sec}; \\ T_0 &= 341.5^\circ\text{K} = 68.5^\circ\text{C}; & k_{d,o} &= 2.8 \times 10^{-5} \text{ 1/sec}; \\ k_{t,o} &= 3.9 \times 10^7 \text{ 1/mol sec}; & h_d &= 14.0 \times 10^{-4} \text{ 1/sec}; \\ h_t &= 1.05 \times 10^{-4} \text{ 1/sec}. \end{aligned}$$

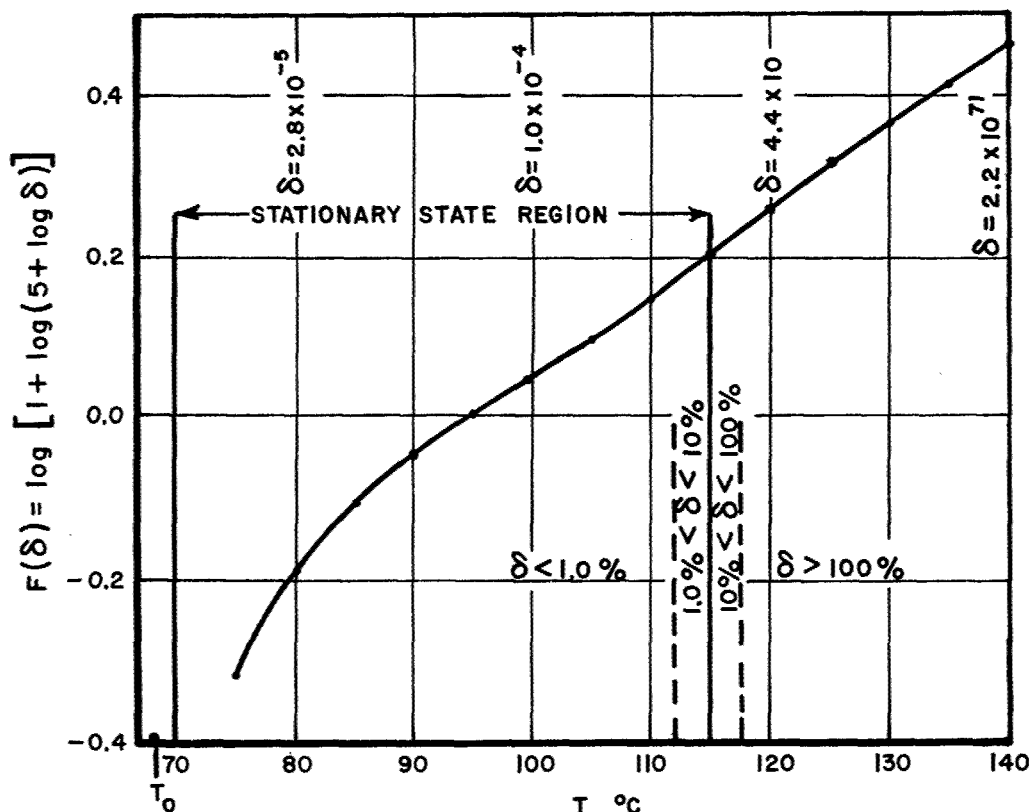
The functions N and δ were calculated from Equation 3. If $T > 115^\circ\text{C}$ the values of δ increase so rapidly that even the plot of $\log \delta$ vs. $t(T)$ could not be drawn because of technical reasons. Therefore, also the following arbitrary function of δ : $F(\delta) = \log [1 + \log(5 + \log \delta)]$ was calculated, and this function provides a convenient plot.

From these results it is evident, that the stationary state assumption can be justified only if T does not exceed 115°C . In such a case the maximum error $\delta < 10\%$. If $T < 112^\circ\text{C}$, $\delta < 1\%$. Therefore, the discrepancy between the expected plot and the observed one of $\ln r$ vs. $t(T)$, which occurs already at $100^\circ\text{C} < T^* < 105^\circ$ cannot be attributed to stationary state assumptions, and other still unknown factors cause this deviation.

The precision factor N , maximum error δ , and $F(\delta) = \log[1 + \log(5 + \log \delta)]$, calculated from the Stationary State Criterion for polymerization of styrene in AIBN by means of DTA are summarized below:

<u>T°C</u>	<u>t(sec)</u>	<u>N</u>	<u>δ</u>	<u>F(δ)</u>
$T_o = 68.5$	0	-	-	-
75	633	4.97×10^4	2.01×10^{-5}	-0.317
80	1120	3.55×10^4	2.82×10^{-5}	-0.185
85	1607	2.47×10^4	4.05×10^{-5}	-0.106
90	2093	1.64×10^4	6.09×10^{-5}	-0.048
95	2580	1.00×10^4	9.96×10^{-5}	0.000
100	3067	5.07×10^3	1.97×10^{-4}	0.046
105	3554	1.81×10^3	5.53×10^{-4}	0.094
110	4041	3.23×10^2	3.09×10^{-3}	0.145
115	4528	1.43×10	7.01×10^{-2}	0.200
120	5015	2.29×10^{-2}	4.37×10	0.261
125	5501	5.46×10^{-7}	1.72×10^6	0.312
130	5988	1.64×10^{-16}	6.11×10^{15}	0.365
135	6475	3.23×10^{-35}	3.09×10^{34}	0.415
140	6962	6.45×10^{-72}	2.24×10^{71}	0.460

Validity of Stationary State Assumption. Polymerization of Styrene in AIBN by means of DTA.
 δ = Relative Error Caused by Stationary State Assumption.



2. Differential Thermal Analysis of Solution Reactions

Investigations by this laboratory to develop techniques of differential thermal analysis (DTA) for use in studies of solution polymerization have continued. The details of apparatus construction to measure the thermal energy evolved in chemical reactions occurring in an increasing thermal environment have been reported previously (Reference 3). Theoretical treatment of the kinetics of free radical polymerization applicable to this system has led to the derivation of rate equations and enthalpic parameters (Reference 4). This report describes the continuation of work undertaken to furnish experimental evidence for determining the applicability of the technique and the proposed theory. The problems encountered in obtaining quantitative data for polymerization reactions by DTA are discussed.

The cell constant, K , for the reaction cell in the DTA apparatus was determined by electrical means. Conventionally, the cell is calibrated by measuring the heat of a known reaction isothermally, usually at room temperature. In order to determine whether the value of K varied as a function of the bath temperature, calibration was carried out over the temperature range normally covered in the experimental work. The following set-up shown in Figure 1, was utilized for the calibration. By this arrangement a known amount of heat could be generated in the reactor cell for calibration measurements. It was found (See Figure 2) that the cell constant K was temperature dependent, increasing by approximately 19 percent over the temperature range 75° to 120°.

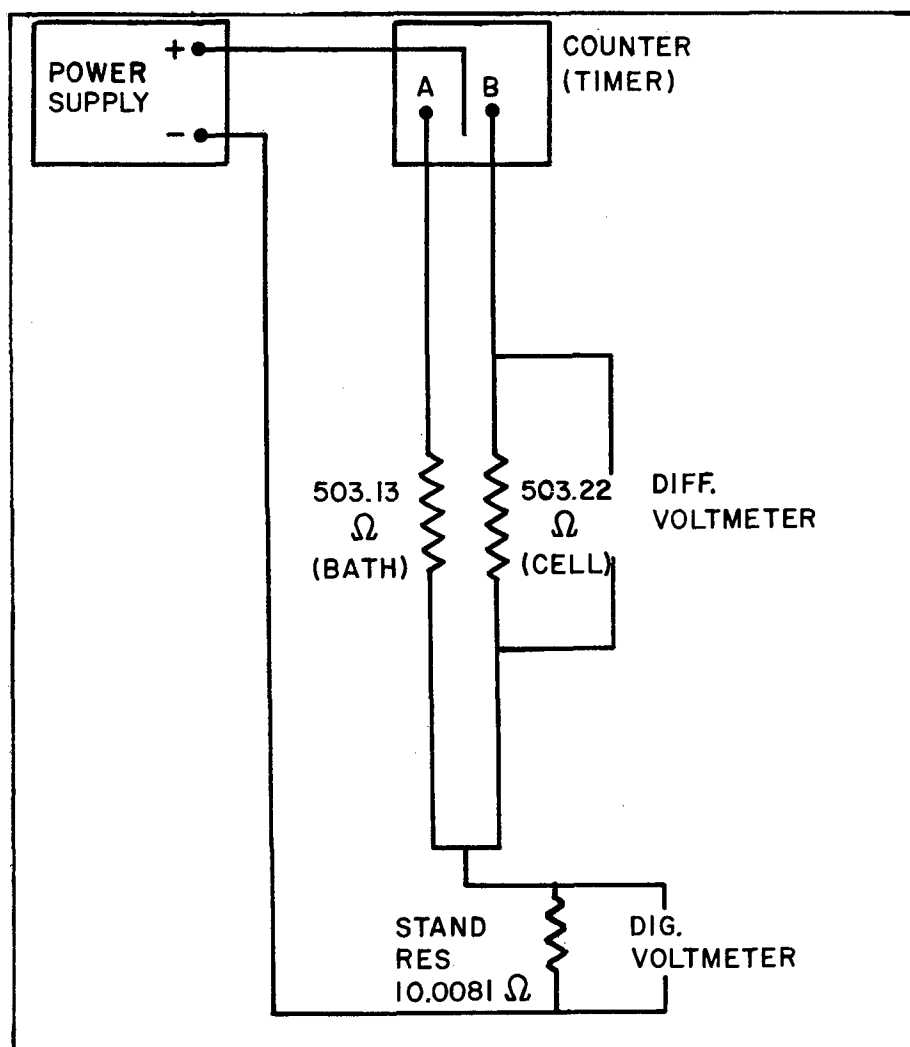


Figure 1. Cell Calibration Diagram

The rate equation for a free radical initiated polymerization for this system has been derived previously (Reference 4). This equation was modified to account for the temperature dependence of the cell constant:

$$\frac{k_p}{k_t^{1/2}} = \frac{CK\Delta T}{(M_0L - P\ell) \left(\frac{K\Delta T'}{A'} \right)^{1/2}}, \quad (4)$$

where

C =reaction constant ($m^{1/2}\ell^{1/2}$), K =cell constant cal/°C sec, T =reaction temperature (°C), M_0 =monomer concentration (m), P =polymer concentration (m), L =total area under curve (cal), ℓ =partial area up to time t (cal), and $K\Delta T'/A' =$ the initiator decomposition rate, $dI_2/dt(\text{sec}^{-1})$.

A series of isothermal experiments was carried out to determine the rate of AIBN decomposition at various temperatures in diethylphthalate. Isothermal runs

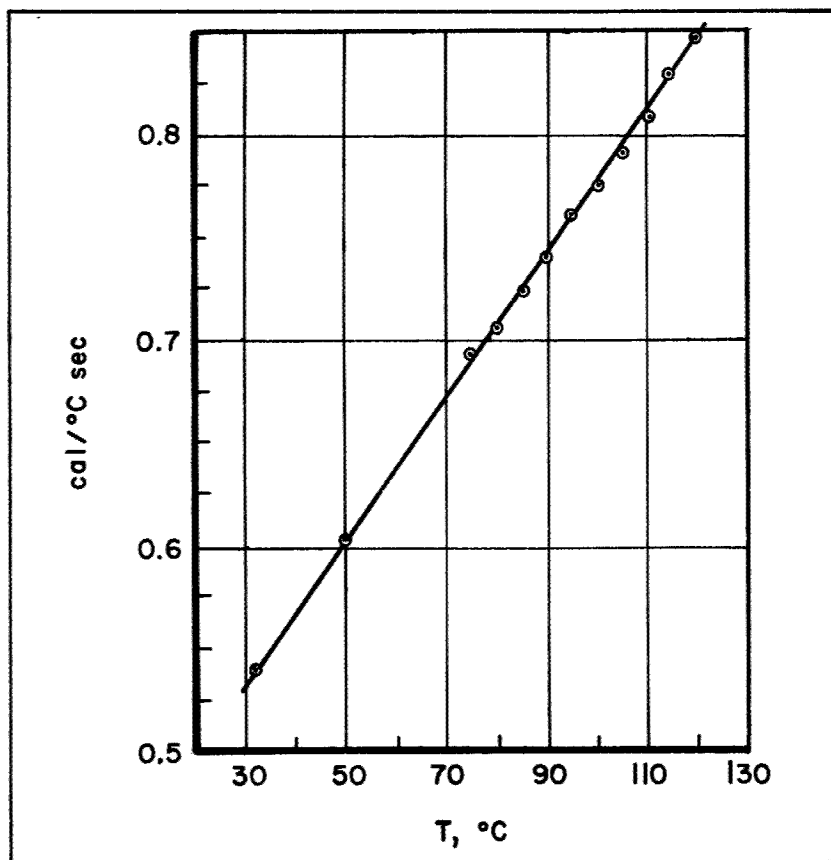


Figure 2. Cell Constant Calibration

were made under a blanket of nitrogen at temperatures ranging from 70-90°C in the following manner: The AIBN was quickly dissolved in the solvent at 40-45°C. The solution of initiator was then transferred to a jacketed microburette which was located above and connected to the reaction cell. After 2 minutes had elapsed to allow temperature equilibrium, a measured quantity of the solution was delivered into the reaction cell and the thermogram recorded. The stopcock and the adjacent non-jacketed parts of the burette were externally heated with heating tape which was adjusted so as to minimize temperature gradients upon addition of the solution to the reaction cell. The curve, ΔT as a function of time, was recorded for each isothermal run. The area under the curve constituted a measure of the heat generated during the reaction.

The total area under the curve, A , is proportional to the total amount of AIBN decomposed. The area generated up to any time, t , is a . The remaining area, $A-a$, is proportional to the concentration, c , of unreacted AIBN. If the initial concentration of AIBN is designated as c_0 , then at the end of the reaction when the initiator is entirely decomposed $c_0 \propto A$. At any time during the reaction $A-a/A$ is therefore proportional to c/c_0 .

The heat evolved by the reaction at any time, measured as the temperature differential ΔT , is proportional to the rate of initiator decomposition, $-dc/dt$. Thus, the rate constant for the decomposition reaction can be expressed as:

$$k = \frac{-dc/dt}{c} \propto \frac{\Delta T}{A-a} \quad (5)$$

or:

$$-\ln \frac{A-a}{A} = kt \quad (6)$$

where rate constants can be determined from the slopes of $\log (A-a)/A$ vs. t plots, in the usual manner.

The experimental data from AIBN decomposition experiments obtained and treated in the manner described above did not prove satisfactory since there was significant scatter of points in the resulting slope plots. The use of xylene as a solvent, repeated recrystallization of AIBN, and special care to exclude air did not improve the reproducibility. The amount of initiator solution that could be added to the cell without producing detectable temperature changes was very small and seriously limited the quantity of AIBN that could be used in an experiment. This required high recorder signal amplification (full scale deflection = $10 \mu V$) in order to obtain curves of suitable size. The resulting increase in recorder noise and fluctuation contributed significantly to the scatter of data. In addition, the control of bath temperature was not entirely adequate for the stringent requirements of this system. The problems associated with isothermal AIBN reactions at these temperatures have not yet been resolved, and that aspect of the work was terminated.

Several AIBN decompositions and styrene polymerizations were carried out using the usual DTA conditions. The heating rate employed was approximately $0.77^\circ C/min$. Diethyl phthalate (100g) was used as the solvent in all cases. All runs were made under a nitrogen blanket.

In the AIBN runs, generally 1.50 grams of AIBN was used. The rates were measured as mentioned earlier (Equation 5). The results of six runs in terms of $K \Delta T/A$ are listed in Table I, along with the mean values and percent deviation from the mean. In the styrene polymerizations (Equation 4) about 13 grams of monomer and 0.07 grams of AIBN were used. Conversion of monomer to polymer was 20 to 25 percent. Rates in terms of $K \Delta T/A$, are listed in Table I.

The reproducibility of data for styrene are considerably better than that for AIBN with the exception of the data obtained from the central region of the AIBN curve where the reproducibility is of approximately the same order as that of styrene. The reasons for obtaining better styrene data are not presently understood. The opposite trend might have been expected in view of the known complexities of polymerization reactions in addition to the possibilities of either inhibition by oxygen, contamination, or loss of monomer by volatilization during transfer to the cell, or during the run.

When these AIBN data were used in calculating the rate constants for the styrene polymerization (Equation 4), the Arrhenius plot exhibited curvature at temperatures above $105^\circ C$ as shown in Figure 3. This apparent decrease in the reaction rate, obtained with increasing temperature, could not readily be explained by a random scatter of the AIBN data alone inasmuch as the curvature of this plot appeared smooth and definitely biased in one direction.

After repeated failures to obtain a linear Arrhenius plot, attempts were made to determine the cause of this deviation from linearity. Accepted literature data (Reference 5) were used to calculate the correct $k_p/k_t^{1/2}$. These rate constants were then inserted in Equation 4 and the equation was solved for the initiator contribution. This AIBN contribution, $K \Delta T'/A'_{calc.}$, is compared in Table II with the experimental mean values. The difference between calculated

TABLE I. REPRODUCIBILITY OF DTA DATA

$$K\Delta T/A \text{ (x}10^4 \text{ sec}^{-1}\text{)}$$

	AIBN								Styrene					
	Run No.	33	34	35	36	40	43	\bar{x}	%Dev	34	35	36	\bar{x}	%Dev
T°C														
80		0.61	0.77	0.82	0.84	0.95	1.06	0.84	13.1	1.04	1.05	1.08	1.06	2.5
85		1.34	1.46	1.64	1.68	1.79	1.72	1.60	8.8	2.01	1.98	1.98	1.99	0.7
90		2.50	2.61	2.51	2.68	2.79	2.66	2.62	3.0	2.91	2.85	3.04	2.93	2.4
95		4.52	4.49	4.36	4.34	4.29	4.44	4.41	1.8	4.29	4.15	4.22	4.22	1.2
100		6.02	5.98	5.55	5.79	5.75	5.77	5.81	2.2	5.22	5.17	5.08	5.16	1.0
105		6.00	5.61	5.41	5.61	5.80	5.61	5.67	2.6	5.22	5.25	5.00	5.16	2.0
110		2.92	2.57	2.31	2.61	2.85	2.75	2.67	6.4	3.14	3.03	2.98	3.05	2.0
115		0.44	0.27	0.32	0.47	0.45	0.52	0.41	19.5	0.72	0.71	0.75	0.73	1.7

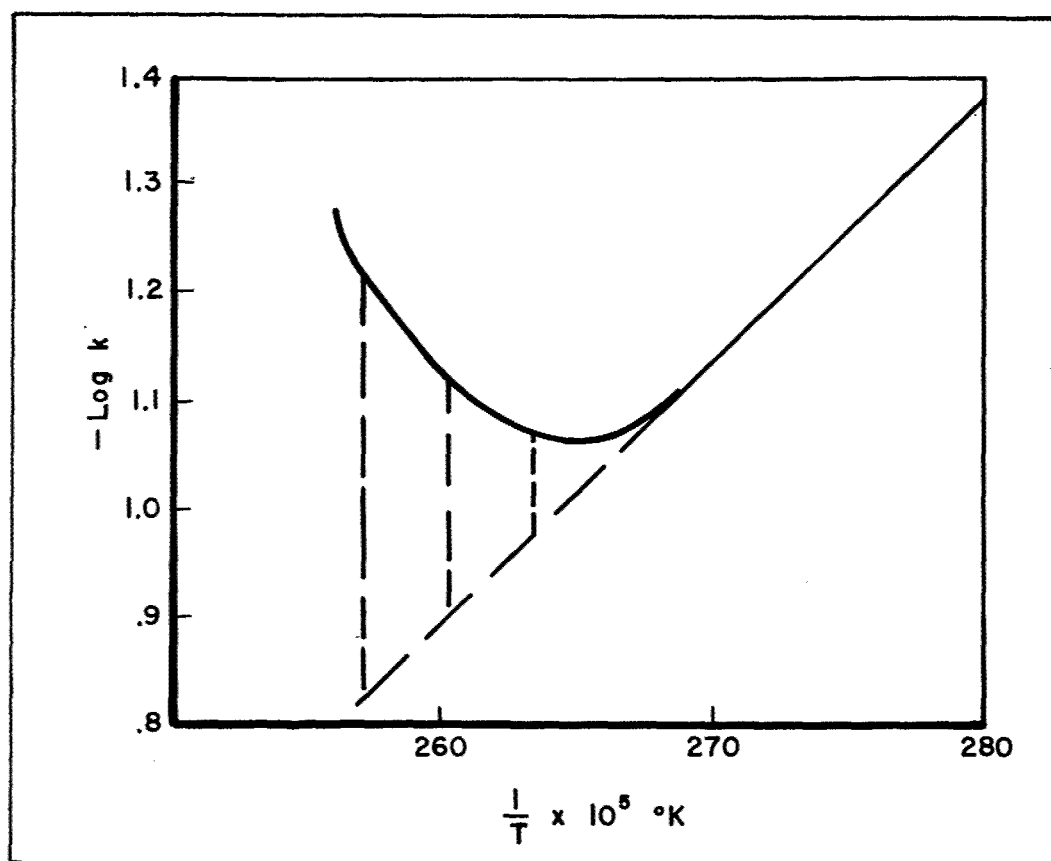


Figure 3. DTA Arrhenius Plot for Polystyrene

TABLE II. CALCULATED $K \Delta T' / A'$ VALUES^(a)

Temp. °C	Calc. ^(b)	Exp. ^(c)	Exp. - Calc ^(d)
80	0.46	0.84	0.38
85	1.30	1.60	0.30
90	2.19	2.62	0.43
95	3.88	4.41	0.53
100	5.24	5.81	0.57
105	4.93	5.67	0.74
110	1.49	2.67	1.18
115	0.66	0.41	-0.25

(a) $\times 10^4 \text{ sec}^{-1}$
 (b) $K \Delta T' / A'$ values, calculated, using Equation 4 and literature rate constants
 (c) $K \Delta T' / A'$ mean values, obtained in DTA experiments. See Table I.
 (d) Difference between experimental and calculated values.

and experimental values failed to disclose a simple relationship. On this basis the experimental $K \Delta T' / A'$ at 110° was found to be almost twice as much as the calculated value.

In view of these discrepancies, an attempt was made to determine $K \Delta T' / A'$ values by use of an equation previously derived (Reference 4) in which the rate constant is expressed in the form of an expanded Arrhenius equation. The initiator decomposition rate, dI_2/dt , was accordingly expressed as $k_d[I_2]$, where

$$k_d = A_d \exp \left\{ -\frac{E_d}{RT_0} + \frac{E_d dt/dt}{RT_0^2} t \right\} \quad (7)$$

and

$$[I_2] = I_0 \exp \left\{ -\int_0^t k_d dt \right\} \quad (8)$$

Denoting $A_d e^{-E_d/RT_0}$ as B_d , and $\frac{E_d dt/dt}{RT_0^2}$ as h_d and rearranging:

$$\frac{dI_2}{dt} = I_0 B_d \exp \left\{ h_d t - \frac{B_d}{h_d} (e^{h_d t} - 1) \right\} \quad (9)$$

where A_d = frequency factor, E_d = activation energy, T_o = temperature at which reaction visibly starts, dT/dt = heating rate.

By means of Equation 8 it was possible to calculate the initiator decomposition rate constants for any combination of E_d , A_d , dT/dt , and T_o . Such calculations were carried out using experimentally obtained AIBN data ($E_d=32.3$ Kcal, $A_d=6 \times 10^{15}$) as well as literature values ($E_d=30.9$, $A_d=2 \times 10^{15}$) (Reference 6). Since the rate of decomposition of the initiator, dI_2/dt , is also $K \Delta T/A$, the results of these calculations could be directly inserted in the polymerization rate Equation 4. This was carried out for 2 styrene polymerizations (#35, 36) and the data are in Table III.

These data indicate that the styrene rate constants are very sensitive to relatively small changes in the $K \Delta T/A$ data. The experimental data indicated once again the previously described decrease in reaction rates at the higher temperatures, whereas the use of the literature values resulted in a linear Arrhenius plot, although the activation energy was twice the literature value, and the frequency factor was in the range $> 10^5$.

A set of AIBN data with activation energies ranging from 30.0 to 37.5 kcal in 500 cal. intervals and three frequency factors (1×10^{15} , 5×10^{15} , 1×10^{16}) were then fed into a digital computer using Equation 9 to compute rate constants for three styrene runs (#34, 35 and 36). The results showed that only one particular set of AIBN data ($E_d = 30.5$ kcal, and $A_d = 1 \times 10^{15}$) in this range produced a linear Arrhenius plot for styrene. All other calculations resulted in curved E_a plots, that is, rates that either increased or decreased. The activation energy for styrene, as determined from this straight line plot was, however, 12.6 kcal, or roughly twice the literature value. A summary of the computer results is given in Table IV.

An additional set of data was then used in which the range of E_d and A_d was extended to 35.0 kcal and 5×10^{17} , respectively. Preliminary evaluation of the data indicates that the

TABLE III. CALCULATION OF POLYSTYRENE RATE CONSTANTS^(a)

	Styrene Run No.			
	35	36	35	36
Temp. °C	A ^(b)		B ^(b)	
80	4.86	4.68	4.02	3.14
90	7.15	7.37	6.14	5.37
100	8.62	7.94	8.23	7.23
105	8.65	7.41	9.52	9.12
110	7.32	5.90	10.7	12.5
(a) the rate constants, $k_p/k_t^{1/2}$ ($\times 10^2$) are in $l\ m^{-1}sec^{-1}$.				
(b) A: using AIBN decomposition rate constants experimentally obtained B: using AIBN decomposition rate constants from literature				

TABLE IV. COMPUTER RESULTS

		E_d , (kcal)					
		30	30.5	31.0	31.5	32.0	32.5
I(a)	E_a , kcal	28.6	12.6 ^(b)	C ^(c)	C	C	C
	Rate	H ^(d)	H	-	-	-	-
II(a)	E_a , kcal	244	120	55	14.4	6 ^(e)	C
	Rate	H	H	H	P ^(f)	P ^(f)	-
III(a)	E_a , kcal	71	103	124	57	22	6 ^(c)
	Rate	H	H	H	H	H	P ^(f)
<p>(a) I: $A_d = 1 \times 10^{15}$, II: $A_d = 5 \times 10^{15}$, III: $A_d = 1 \times 10^{16}$</p> <p>(b) This is the only combination resulting in a linear Arrhenius plot for styrene.</p> <p>(c) C: Activation energy plot curved. Rate slows with increasing temperature</p> <p>(d) H: Rate constants excessively high</p> <p>(e) These combinations of E_d and A_d are similar to and reproduce the experimental results.</p> <p>(f) P: E_a is straight to 105°, then curves. Activation energy determined from straight part of plot.</p>							

styrene data appear to be very sensitive to relatively small changes in the initiator data. The curvature of the activation energy plot appears to be a function of the proper ratio between E_d and A_d . Thus, in the limited range of data used here, a straight line plot is obtained whenever $E_d/\log A_d = 2.000$ to 2.035 kcal.

Although the experimentally determined rate constants differ from literature values to produce curvature in the Arrhenius plot as shown in Figure 3, it does not appear that experimental error alone can fully account for this. Literature values were obtained for AIBN decomposition by techniques involving measurements of nitrogen evolution (References 7, and 8) and optical densities by ultraviolet absorption (Reference 6). These techniques, in contrast to DTA, are isothermal and are usually confined to temperatures of 80° and below. At the higher temperatures encountered in our DTA work side reactions which do not influence kinetic measurements by the above techniques may be occurring and affecting results. Reactions may be occurring, which while contributing heat may not produce the proportion of chain initiating radicals expected and thus give a falsely high value for $K \Delta T' / A'$. Such phenomena may be responsible for the presently unexplained discrepancies.

3. Kinetics of Cyclopolymerization

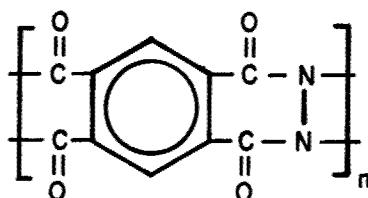
This laboratory has had considerable interest in elucidating mechanisms of cyclopolymerization (Reference 9). A method and the related theory have been developed to determine the relative rate constants of competing reactions in such systems by VPC analysis of chain transfer systems (Reference 10). VPC data from several experiments have been collected, however treatment of this raw data is incomplete. Upon completion, the experimental results, calculations to evaluate rate constants, and conclusions derived from this work will appear as Part II of the previous report (Reference 10).

SYNTHESIS OF LADDER STRUCTURE IN POLYMERS

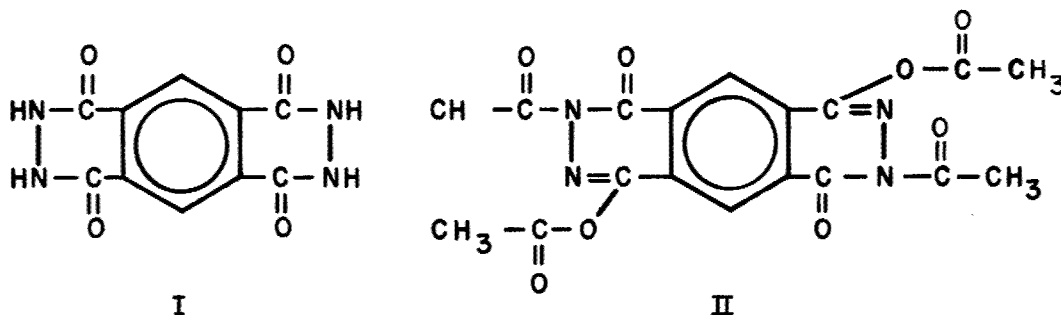
During recent months, interest in the preparation of polymers containing backbone ladder structure has continually increased. With the exception of the Phenyl-T polymer (cis-syndiotactic polyphenylsilsesquioxane, discussed later in this report), well identified ladder polymers are unavailable for characterization studies. When available, ladder polymers are expected to give rise to a new class of materials with unique and useful properties. For this reason, effort in this laboratory is being spent in an attempt to synthesize these novel substances.

1. Polyhydrazide System

Since the last report, (Reference 9, Report V) additional attempts have been undertaken to prepare a ladder polymer having the structure:



The monomer, sym-pyromelleyldiazine-2,3,7,8-tetrahydro-1,4,6,9-tetrone (I) is insoluble in solvents



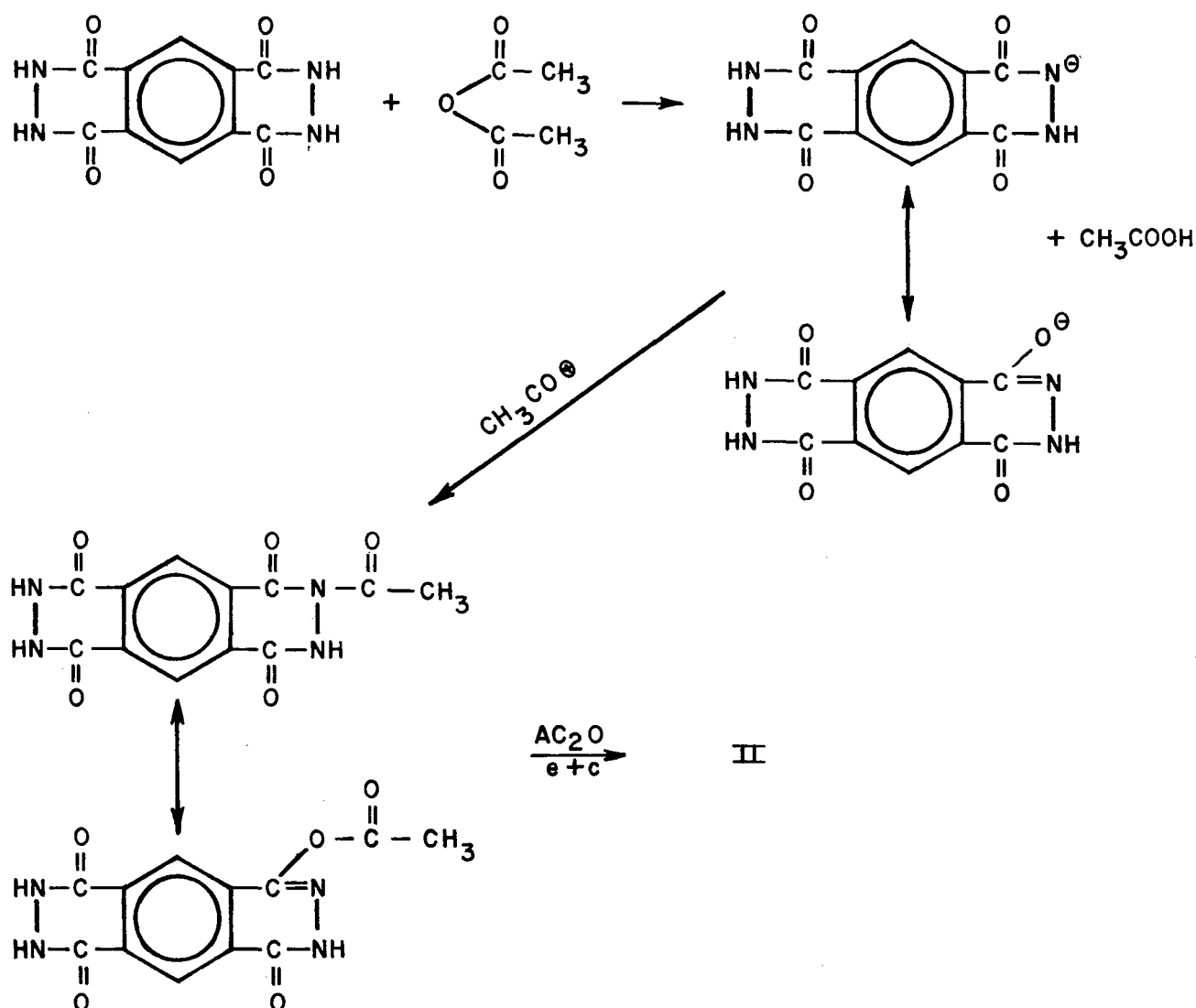
suitable for polymerization. The tetra acetyl derivative (II) showed an enhanced, although still poor, solubility in polar solvents. A number of approaches were undertaken to circumvent this difficulty.

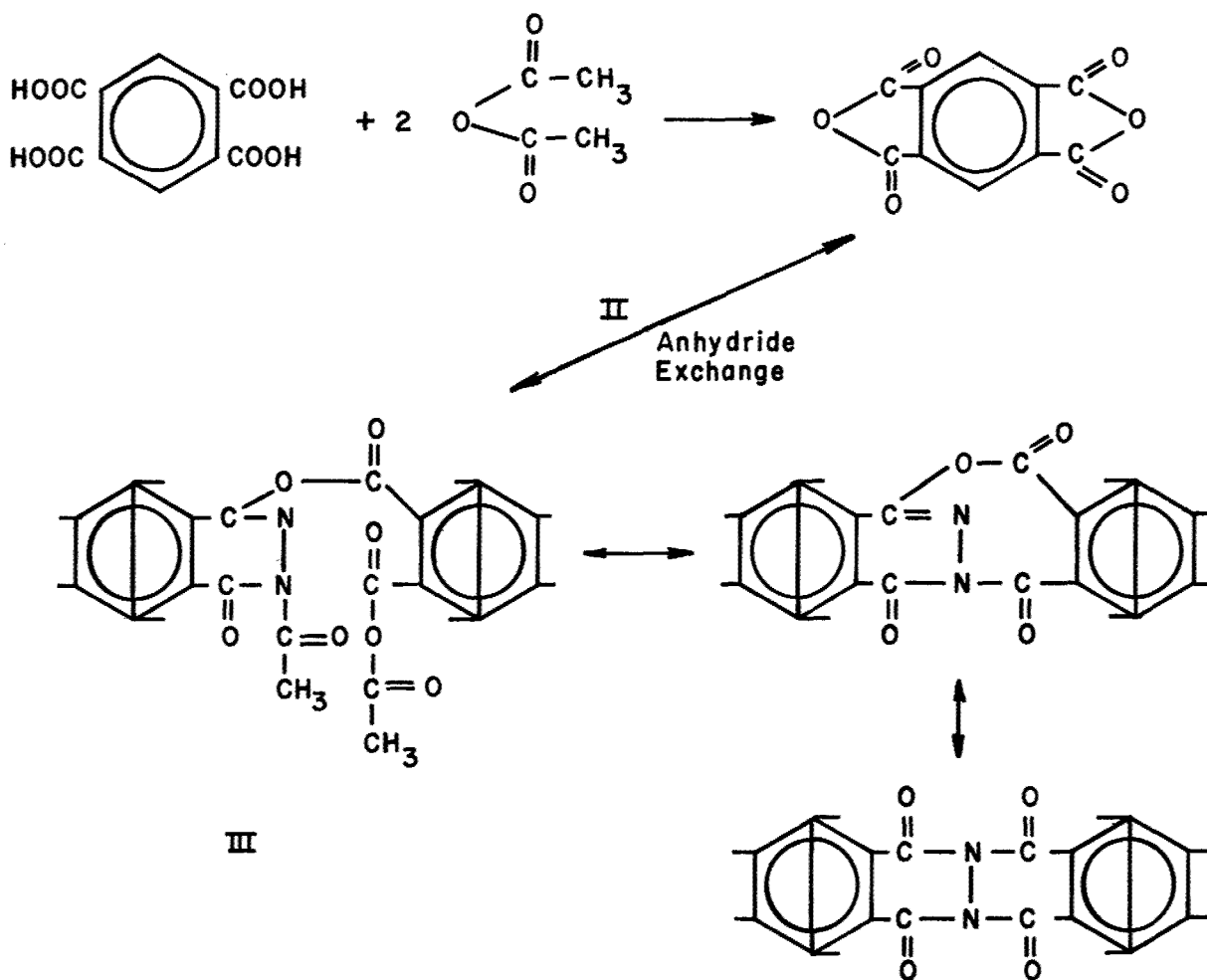
Use of the highly reactive tetraphenyl ester of pyromellitic acid was made. Tetraphenyl pyromellitate, prepared by the reaction of pyromellitoyl chloride and phenol under anhydrous conditions was reacted with the dihydrazide (I). This reaction affords maximum exploitation of the acidic hydrazide hydrogens while being essentially a non-equilibrium process. Reactions were conducted in both melt and solution phases but with no success. Degradation occurred under the conditions (200°C) necessary for a melt polymerization and no reaction was effected in dioxane at 101°C.

The sym-tetraacetyl pyromelletyl dihydrazide (II) and pyromellitoyl chloride were reacted. In this system, the volatile elimination product (acetyl chloride) could be rapidly removed thereby insuring the maximum reaction rate consistent with the system solubilities. After three days in refluxing dioxane only a small amount of dimer had formed.

Polymerizations using a reactive solvent were attempted. This approach utilizes highly polar solvents and in this way minimizes the solubility problems.

For the system pyromelletyl dihydrazide (I) - pyromellitic acid - acetic anhydride, the reaction path may be indicated as:

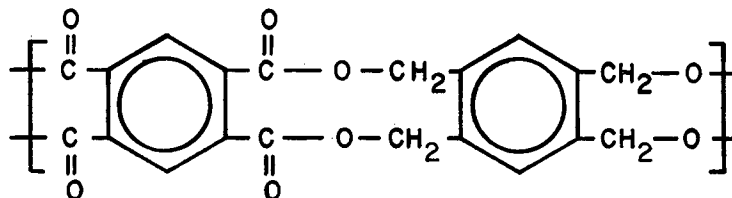




Since the anhydride exchange should be an equilibrium step, it was necessary to slowly remove the acetic anhydride which would be expected to compete with the pyromellitic anhydride in the reaction. It was found that little reaction occurred so the first anhydride exchange step was incomplete or the sterically hindered intermediate (III) reverted to the tetra acetyl derivative and pyromellitic anhydride. A probable reason for this failure is the likelihood of stable five membered ring formation. A similar reaction scheme was undertaken in which thionyl chloride was substituted for acetic anhydride as the solvent. In this case no reaction occurred due to the complete insolubility of the dihydrazide (I) in this solvent. Since the polyhydrazide ladder system was unobtainable by these approaches, research effort on this system was terminated.

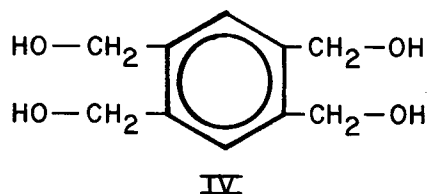
2. Polyester Systems

Research effort has been directed toward esterification reaction systems which utilize soluble monomers and if successful should lead to easily characterizable polymers having the structure:

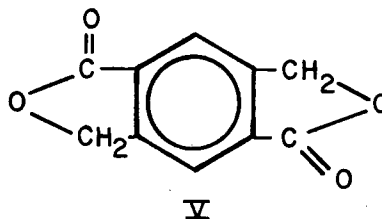


Such a polymer would not be expected to exhibit superior thermal stability because of the probable tendency to form pyromelletic anhydride and products arising through hydrogen abstraction of the active methylene groups present. Such a polymer would, however, be extremely valuable for elucidating the properties of ladder type macromolecules.

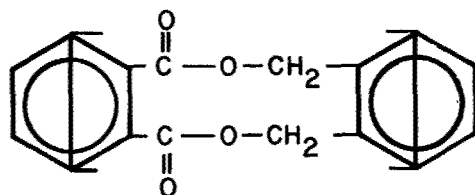
This system involves the condensation of pyromelletyl alcohol with pyromelletic acid (or anhydride or acyl chloride). Pyromelletyl alcohol (1,2,4,5-benzene tetra methanol) (α , α' , α'' , α''' tetra hydroxy durene) (IV),



was prepared by the reduction of pyromelletic anhydride with lithium aluminum hydride in 63 percent yield. Side reaction products consisted of partially reduced anhydride and the dilactone V.



This lactone structure is not readily polymerized. No linear esters were obtained as reduction products and no polyesters could be formed from deliberate polymerization attempts. The five membered lactone ring is considerably more stable than the 10 membered cyclic diester:

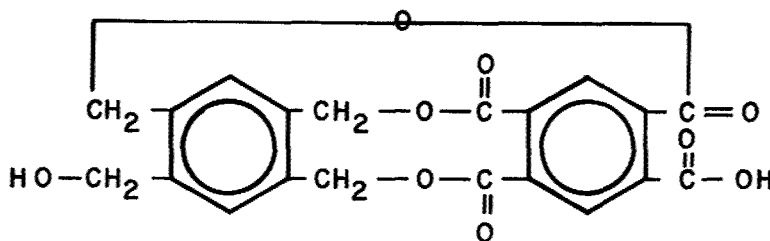


This behavior was certainly not unexpected, and its significance will become apparent in the discussion to follow.

Having prepared and purified the alcohol (IV) (M.P. 191.9-193.9°C) by recrystallizations from dioxane, a polymerization was attempted. Figure 4 shows the progress of the reaction between pyromelletyl alcohol and pyromelletoyl chloride in dioxane as measured by the hydrogen chloride evolution (as silver chloride). This reaction was conducted at 101°C in refluxing dioxane for 2 weeks but gave only 75 percent of the theoretical yield of HCL. This result was not anticipated since an alcohol and an acyl chloride would be expected to react rapidly and almost quantitatively.

The viscosity of the pale yellow ester obtained was 0.06 dl/gm while the elemental analysis was consistent with a tri-ester. Figure 5 shows the thermal gravimetric analysis curve.

The soluble "polymer" gave the proper infrared spectrum with ester bands at 5.82, 8.0-8.1, 8.98 and 9.15u. Upon hydrolysis both the alcohol and the potassium salt of the acid were isolated and identified by their infrared spectra. Elemental analysis ($C_{20}H_{15}O_9$) corresponded to the tri cyclic structure;



where the acid group could arise through hydrolysis of the $-C(=O)-Cl$ group on isolation.

Because of the intensity of the infrared absorption due to the ester groups, the carboxylic acid groups and the alcohol groups could be marked. The preceding structure is consistent with the polymerization curve (Figure 4), as only 75 percent of the chlorine would be consumed. It is also in agreement with the equivalent molecular weight of 95 obtained through titrations

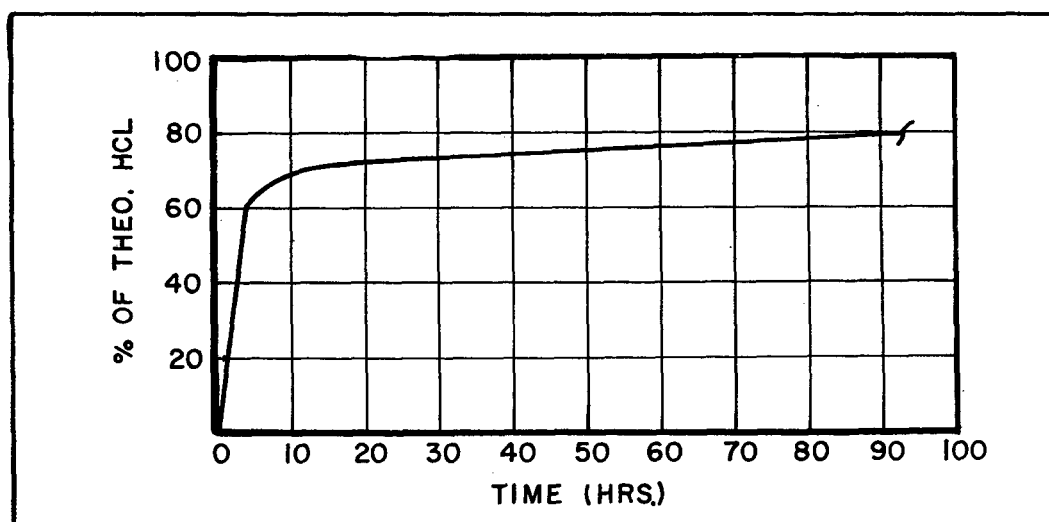
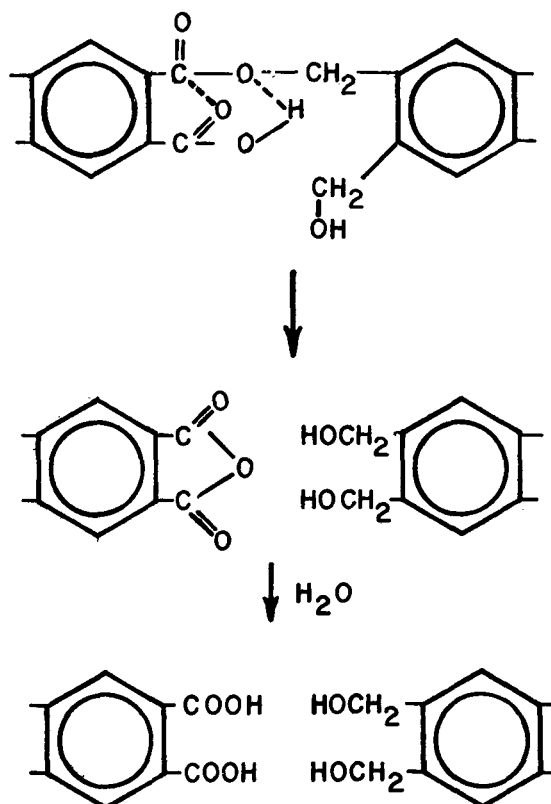


Figure 4. % Reaction vs. Time for a Polyester Polymerization in Dioxane at Reflux

with alcoholic potassium hydroxide. Hydrolysis of this structure would give an equivalent molecular weight of 99. Such hydrolysis could easily occur through a "push-pull" mechanism (Reference 11) such as:



The tricyclic structure was not expected because of the ring strain involved. A larger ring, consisting of four benzene residues would also correspond to the experimental observations,

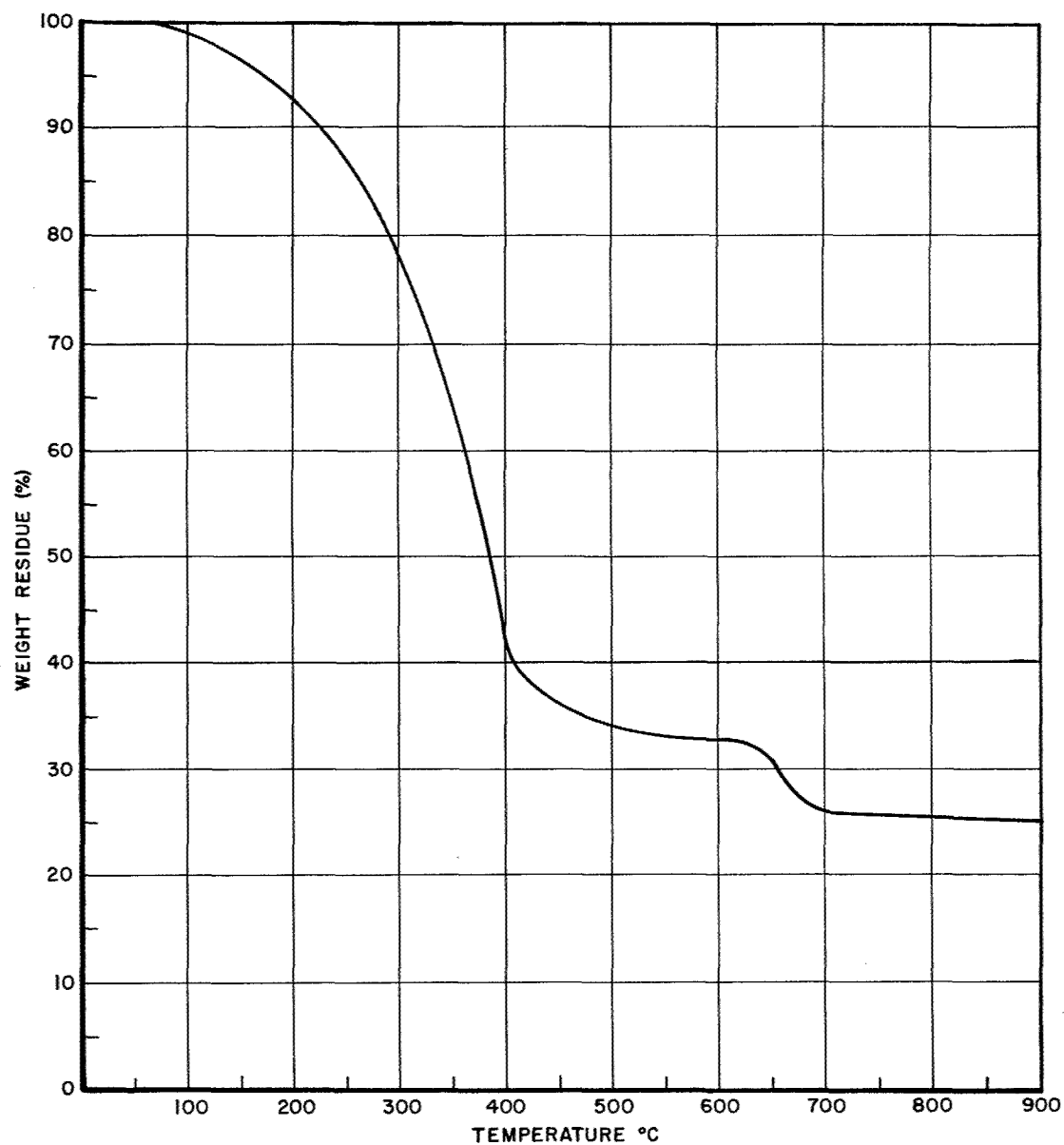


Figure 5. Thermal Gravimetric Analysis of the Mono Ester of Pyromelletyl Alcohol and Pyromellitoyl Chloride
 $\Delta T=150^{\circ}\text{C}$ 1 hr.

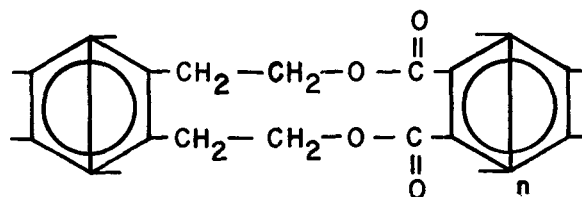
however, the probability of ring closure in such a system would be remote. No insoluble (network) material was formed. This observation indicates the absence of random reaction, and the very low viscosities preclude any significant polymer formation. In support of the proposed structure, one other property may be mentioned, and this is the extensive cross-linking of the isolated material upon vacuum drying at 80°C. This rearrangement is not only reasonable but would be expected from such a strained system.

Figure 6 shows the viscosity vs. temperature of reaction relationships for a few polymerizations. The viscosity never exceeds 0.067 dl/gm. Figure 7 shows essentially no viscosity change with time at a reaction temperature of 200°C. Reactions have been conducted for as long as two weeks with no significant change. As the reaction temperature is increased, the elemental analysis values deviate from any reasonable structure and the infrared curves become complex and inconsistent with the expected reaction. Between 200 and 250°C decomposition begins (Table V). Even at this temperature the C/H ratio is far from that of a polyester. A Fisher-Herschfelder-Taylor molecular model indicates the normal bond rotations to be hindered due to the carbonyl groups. If this is the case, ring opening should occur at a low temperature.

TABLE V. ESTER LINKAGE DECOMPOSITION

Temp. (°C)	101	150	200	250	Theo.
%C	54.4	58.8	61.3	68.5	63.2
%H	4.14	4.74	4.59	4.67	3.18
%O	41.5	36.5	34.1	26.8	33.7
C/H	13.1	12.4	13.4	14.7	19.8

Freshly sublimed benzoquinone was added to a polymerization mixture at 200°C to check for the possibility of a radical degradation process. Both hydroquinone and its pyromellitic esters were isolated. A blank run (without pyromellitic acid) gave no hydroquinone. From these results it would appear that the 10 membered ring, once formed, can rupture homolytically. The occurrence of these free radicals explains the strange elemental analysis values. The existence of a large degree of strain in the 10 membered ring also explains the low reactivity of this system, the low viscosity values, and adds support to the tri-ester structure postulated above. The lack of an electron spin resonance apparatus precludes complete proof of the proposed radical degradation. As a result, efforts are presently being made to prepare the structure:



This 12 membered ring should show more flexibility than its 10 membered analogue and may thereby lead to a ladder polymer. The probability of ladder formation decreases as the ring size increases because of the enhanced likelihood of crosslinking.

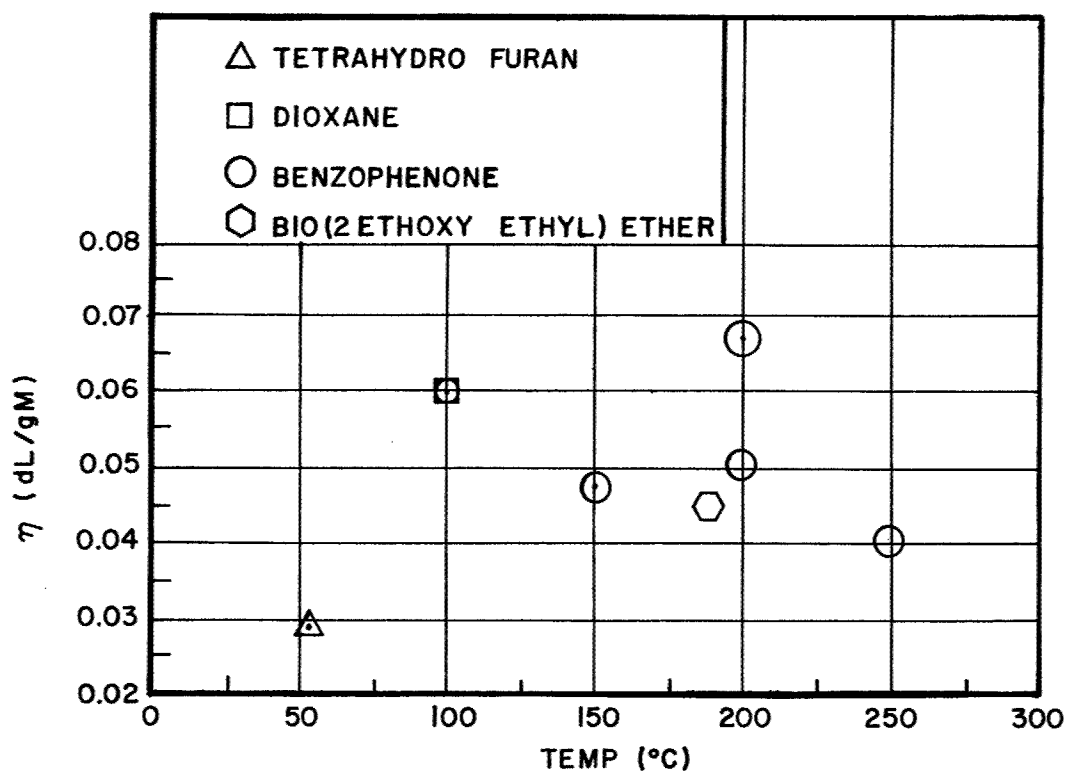


Figure 6. Viscosity of Polyester vs. Reaction Temperature

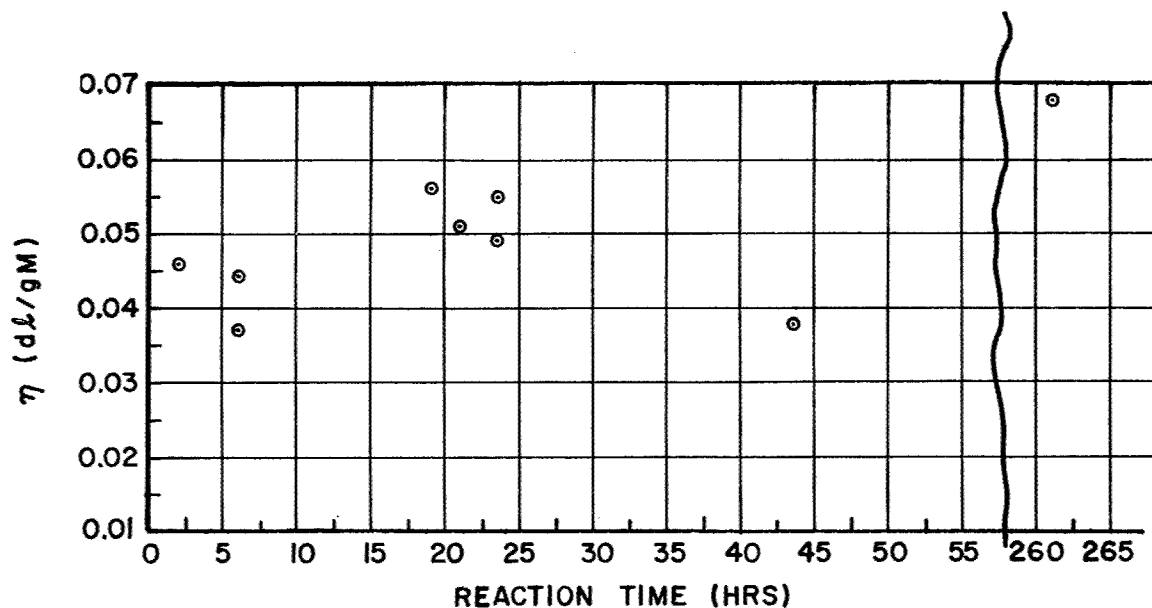


Figure 7. Viscosity vs. Reaction Time at T=200°C

3. Other Systems

During this report period investigations of other systems have been initiated. Preliminary experiments on some systems show promise of producing fused ring structure in polymer backbones. Follow-on investigations are in progress and will be reported in the near future.

INVESTIGATIONS OF MOLECULAR STRUCTURE-PROPERTY RELATIONSHIPS

ULTRACENTRIFUGATION

A new Spinco Analytical Ultracentrifuge, Model E, was installed in the laboratory. This is a multi-component instrument, characterized by high speed and 250,000 G centrifugal field. Preliminary calibration was previously reported in Progress Report V (Reference 9).

1. Instrumentation

In the interest of safety all components were carefully examined and defective parts replaced. Also, additional safety devices were installed to automatically cut off instrument power in the event that water and/or power are not properly supplied to the instrument. Installation of a circulating water cooling system required special plumbing.

The vacuum temperature control and Schlieren Optical systems were adjusted and calibrated. The alignment of the interference and UV absorption optics are now in progress. Other auxiliary components to be utilized on the instrument have not yet been delivered.

Two computation methods, (a) to determine the sedimentation coefficient by the Svedberg method and (b) to determine the diffusion coefficient (Reference 12), were programmed for computer analysis. A new special Kel-F cell is being fabricated for use in investigations of new polymers. In addition, an attempt has been made to develop a new density gradient technique which will be applicable for investigating novel polymer systems. Use of this method requires a special solvent medium compatible with the UV absorption optics detection system. The spectroscopic data of many compounds have been analyzed to make the proper selection of gradient medium. This work is still in progress.

2. Preliminary Measurements on Polystyrene and Phenyl-T

Polystyrene in cyclohexane was investigated at 35°C, the theta temperature. Since all accessory components necessary for good temperature control above 30°C were not available, thermal gradients very often appeared during the runs. Only one of three determinations could be considered to be partially successful. Preliminary calculations led to the following results for this case: $s_0 = 4.22$ sved; $D_0 = 6.85 \times 10^{-7}$ cm²/sec. This investigation will be continued when the high temperature control system is completely installed on the instrument.

Preliminary experiments with Phenyl-T (cis-syndiotactic polyphenylsilsesquioxane) (batch A) in toluene at 12°C were carried out. A technique utilizing the synthetic boundary cell and Schlieren Optics was proven successful. The sedimentation coefficients plotted vs c are given in Figure 8. It was found that $s_0 = 13.04$ sved.

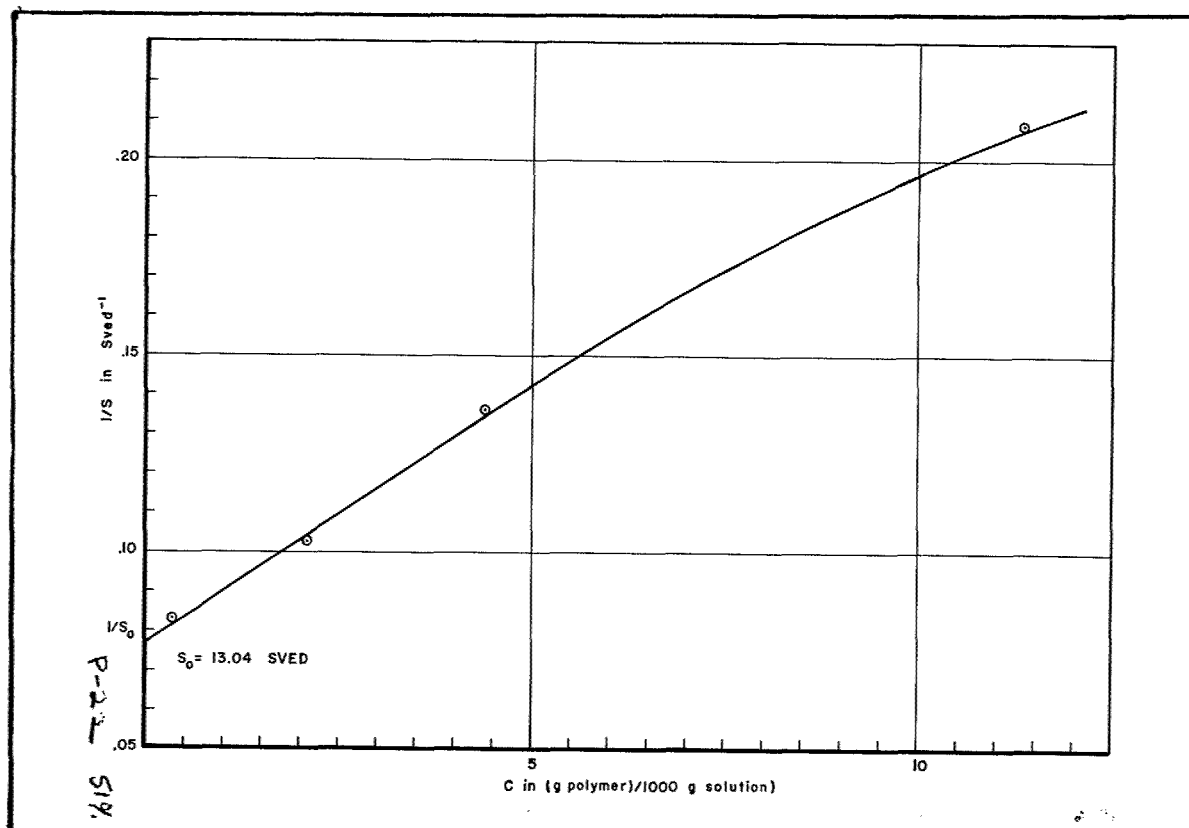


Figure 8. Sedimentation of Phenyl-T-A in Toluene at 12°C

Phenyl-T in toluene appears to be a suitable system for investigation, and this work will be continued in the future.

3. Extensions of Current Theory

(a) Sedimentation at Variable Centrifugal Velocity and Variable Parameters of Flow: An attempt has been made to determine elastic properties of polymers in solution by applying techniques of ultracentrifugation. Since the heterogeneity of the centrifugal field may change the shape of macromolecules, one may expect that the parameters of flow will vary with varying speeds of ultracentrifuge. Therefore, the dependency of the sedimentation and diffusion coefficients upon the centrifugal field may lead to the evaluation of the parameters of elasticity.

The existing expressions for sedimentation were derived under the assumptions of constant angular velocity (w), constant sedimentation coefficient (s), and constant diffusion coefficient (D). Therefore, the suggested investigation calls for additional formulas to describe the new conditions. One can let the angular velocity, and coefficients of sedimentation and diffusion be functions of time defined as: $w = R(t)$; $s^* = s \mathcal{J}(t)$, and $D^* = D \mathcal{D}(t)$, where s and D are the corresponding values of s^* and D^* for $w=0$. Considering the radial displacement, Δr , which a macromolecule undergoes during sedimentation, to be small in comparison with the total radial distance r , the dependency upon the field can be seen to be dependent on the angular velocity alone. Disregarding the influence of the meniscus and the bottom of the cell, the solution of the corresponding new differential equation leads to the following expression for the concentration:

$$C(r, t) = 2 C_0 e^{-2B_e \rho^2} \int_0^\infty u e^{-u^2} I_0(2\rho u) du \quad (10)$$

where: I_0 = zero order complex Bessel function; c = concentration; c_0 = initial concentration; r = distance from the center of rotation; r_0 = distance of the initial boundary; and $\beta = sw^2$;
 $B(t) = \int_0^t \beta(x) dx$;

$$\alpha = \frac{1}{t} e^{2B(t)} \int_0^t e^{-2B(x)} dx; \quad \rho = r/(4D\alpha t)^{\frac{1}{2}}; \quad \rho_0 = (r_0 e^{B(t)})/(4D\alpha t)^{\frac{1}{2}};$$

Since the expressions derived did not require any explicit assumptions for the functions of time, as $B(t)$ and $\alpha(t)$, they are also valid for any special assumption made for w , s , and D . Therefore, a principle of analogy was suggested, which directly transforms all existing formulas into new ones, if derived only by utilizing integrations or differentials with regard to r .

This phase of a broad investigation of sedimentation theory has been reported (Reference 18).

(b) Sedimentation in the Neighborhood of the Meniscus: The existing expressions for sedimentation have been derived assuming that the ultracentrifuge cell is infinitely long. Quantitative ultracentrifugation eliminates the influences of the meniscus and bottom of the cell by application of special "synthetic boundary" techniques. This technique cannot be utilized in cases where the polymer solvent tend to swell the plastic components of the cell itself. Even in those cases where solvent does not present a problem, the influence of the meniscus should not be disregarded. Therefore, an investigation has been carried out to derive expressions describing sedimentation in the neighborhood of the meniscus.

Such a problem is equivalent to the solution of the following differential equation:

$$c_t = D c_{rr} + D \frac{1}{r} c_r - \beta r c_r - 2\beta c, \quad (II)$$

where c =concentration, r =radial distance, t =time, D =diffusion constant, $\beta = sw^2 = \text{const.}$, s =sedimentation constant, and w =constant angular velocity, under the following conditions:

The initial conditions:

$$c = c_0 = \text{const.}, \text{ at } t = 0, \text{ for } r_m \leq r < \infty; \quad (IIa)$$

The boundary conditions at infinity:

$$c = c_0 e^{-2\beta t}, \text{ at any } t, \text{ for } r = \infty; \quad (IIb)$$

The boundary conditions at meniscus (for $r=r_m$):

$$(D c_r - \beta r c) = 0, \text{ for } r=r_m, \text{ at } t > 0. \quad (IIc)$$

Three different methods, which may lead to the solution of Equation 11, were examined as follows: (1) Fourier Method; (2) Solution in Steps; (3) Laplace Transform.

(1) Applicability of the Fourier Method depends upon the existence of some orthonormal series, which can express the function (c) if appropriately transformed. If a new coordinate $x = r^q$ is used for such a transformation, then for $q > 0$, the orthonormalization must be carried out within the integral limits, unity and infinity. Since no such functions are known to the author they must first be found or defined. On the other hand, if $q < 0$, there exists at least the Jacobi-Series which can be normalized under the new conditions within integral limits, zero and unity. Therefore, the basic equation can now be transformed to convert it to the following hypergeometrical equation:

$$x(1-x)u'' + [q - (p+1)x]u' + n(p+n)u = 0, \quad (12)$$

which can be solved by the Jacobi-Series. This calculation is still in progress.

(2) By "solution in steps" it is meant that first one must attempt to obtain a particular solution by simplifying the conditions, and subsequently use this special solution to derive the general expressions. Two different applications of this method are being carried out: Firstly, the sedimentation has been disregarded by assuming $\beta = 0$, and the equation is being solved for the diffusion only. This solution will be then generalized for $\beta \neq 0$; Secondly, an analogical equation for a perpendicular cell with axial symmetry is being solved. This solution is supposed to be extended into a cylindrical field with radial symmetry. This calculation is also in progress, and seems to be promising.

(3) In this approach the basic Equation 11-c was transformed, to make the p-Laplace Transform applicable. Two of such transformations have led to compact expressions for the image $\phi(\chi, p)$. One such expression is:

$$\phi(\chi, p) = 1 + A(p)I_0(\chi, p) + B(p)K_0(\chi, p), \quad (13)$$

where I_0 and K_0 are the well known cylindrical function. The evaluation of $A(p)$ and $B(p)$ is still in progress, and if accomplished an inverse Laplace Transform of the image has to be made. The complete details of this investigation will be described by a technical report published in the near future.

4. New Pycnometers

The determination of molecular weights and sizes of the macromolecules calls for some additional data other than the information obtained from the ultracentrifugation. In all cases, the pycnometric and the viscometric data must be provided. In the application of some special techniques of sedimentation additional information such as that obtained from refractometry, spectrophotometry, and so forth, is also required. Since all measurements must be carried out under identical conditions and the results extrapolated to $C=0$, the need for reliable auxiliary measurements is great, especially those by pycnometry and viscometry at low concentrations.

To increase precision and feasibility of density measurements, new types of pycnometers have been suggested for use (Reference 13), in addition to glass pycnometers newly introduced

to the laboratory. One was chosen to be fabricated and examined. The most significant feature of this new pycnometer is a magnetic float with adjustable density which can be adjusted to a density nearly the same as some reference solution. This float is surrounded by the solution under investigation, and resides in an inhomogeneous electromagnetic field. Automatic control systems shift the float to a constant position dependent upon the solution density and indicate the force required to achieve the displacement. After calibration, differences between the densities of solution and that of the magnetic float can be determined. The following advantages of this new method should be stressed: (a) being influenced by buoyant forces, the float acts as a differential pycnometer which gives rise to the detection of additional weights resulting from differences in concentrations of solutions; (b) the influences of humidity and the atmosphere are eliminated; (c) the need to measure the volume of the solutions or to keep it constant is eliminated; and (d) the automatic control system affords simple operation. Complete details of this newly discovered pycnometer will be described in a separate technical report.

LIGHT SCATTERING

Research specifically directed toward advancing the techniques of light scattering as a means of determining important solution properties of polymers continues. The specially developed light scattering instrument (Reference 9) has been reinstalled in our new laboratory location and recalibrated.

1. Instrumentation

Further improvements made on the light scattering instrument included the following: (a) A new thermostatic cell has been developed (Reference 14). A prototype cell is already in use, and its improved version is being fabricated. (b) A new method of beam splitting which is independent of room temperature has been developed (Reference 15). Use of the original beam splitting device (Reference 9) introduced significant error as a result of room temperature fluctuation. A system of perpendicular windows installed to replace the beam splitter are independent of room temperature changes and seem to provide much better accuracy. (c) Some optical parts, especially the light chopper, masks, slits, and traps for stray light, were improved. (d) The optical bench design was modified to permit the attachment of a laser as an additional light source. The bench modification is now being fabricated. (e) Another improved electrical bridge was introduced, however, this new system can not be examined yet until new EMI photomultipliers which are sensitive to the red light of laser beams are delivered.

SOLUTION PROPERTIES OF PHENYL-T

Investigations of the solution properties of cis-syndiotactic poly-phenylsilsesquioxane (Phenyl-T) are underway to provide fundamental knowledge of substances possessing the ladder structure. The work presented here is a continuation of a previously reported study (Reference 9, Report V) to develop techniques for preparing ladder polymers and characterizing them by the determination of solution properties.

1. Osmometry and Viscosity of Fractionated Polymer Solutions

The results of this phase of the investigation are being reported elsewhere (Reference 16). The following is a summary of these results. Two samples of Phenyl-T polymer, designated PT-A ($[\eta] = 1.35$ dl/gm. benzene 25°C) and PT-B ($[\eta] = 0.95$ dl/gm benzene 25°C), have been fractionated from a solvent-non-solvent system (benzene-methanol) to yield six and ten fractions respectively. Intrinsic viscosity measurements (benzene, 25°C) and osmometry measurements (toluene, 37°C) have provided suitable data to determine the Mark-Houwink equation for Phenyl-T ($[\eta] = 1.595 \times 10^{-5} M^{0.909}$ for benzene at 25°C). From these data, Huggins

constants, K' , have been calculated as well as second-virial coefficients and their variation with molecular weight. In addition, a means of predicting fraction size is presented based on a relationship of polymer concentration and excess non-solvent. The data presented suggest that the Phenyl-T polymer does not behave as a flexible molecule.

2. Theta Temperatures in Various Solvents

The continuation of the search for a suitable theta-solvent for Phenyl-T has yielded three additional candidates; ethylene dichloride, o-xylene and α -chlorotoluene. Measurements have been made for the ethylene dichloride-Phenyl-T system and the data indicate the theta temperature to be in the range of 45°C to 50°C. The large uncertainty is based on the fact that the data obtained was not reproducible. The variation in second virial coefficient with temperature was observed by making the osmometry measurements in Stabin osmometers with apparent equilibrium achieved in twenty-four hours. However, using slow 600 membranes it has become obvious that equilibrium times of at least forty-eight hours are required. Hence, new data is being obtained to eliminate the uncertainty of the theta-temperature for ethylene dichloride-Phenyl-T. Osmometry measurements as a function of temperature will also be made for o-xylene and α -chlorotoluene.

SOLUTION PROPERTIES OF POLYBENZIMIDAZOLE

Much research effort has been spent on the synthesis of the poly-benzimidazoles and as a class of compounds. These materials are currently being used to satisfy Air Force materials requirements. Nevertheless, information concerning bulk and solution properties of these materials is lacking. Consequently, effort has been initiated in these laboratories to elucidate the physical-molecular properties of the various polybenzimidazoles.

1. Ultracentrifugation and Related Measurements

An investigation to measure solution properties of polybenzimidazole (PBI) by its sedimentation characteristics has been initiated. Preliminary density, viscosity and sedimentation measurements have thus far been completed.

A new technique to carry out precise density measurements was introduced. Special glass pycnometers (Reference 17) were fabricated and a temperature control bath ($\Delta T = \pm 0.001^\circ\text{C}$) was built. The following measurements on PBI in DMAC were carried out: (a) Bulk polymer measured at 25°C and 30°C in a concentration range of 0.5%-1.7%; (b) preheated batch measured at 30°C in a concentration range of 0.0-0.5%. From the experimental data the density of solution, ρ , the partial specific volume of the polymer V_p , and the function $1 - V_p\rho$ were calculated and plotted vs c. (See Figure 9)

The following values for $c=0$ were obtained:

$$(V_p)_{c=0} = .649 \text{ cc/g}; (1 - V_p\rho)_{c=0} = .396.$$

The preliminary measurements indicate an abnormal behavior for PBI solutions of low concentrations. These solutions seem to undergo some transition from one state to another. The normal behavior at 30°C could be only recorded for concentrations less than 0.35 percent. To gain additional information on the behavior of PBI, more density measurements at different temperatures are being made.

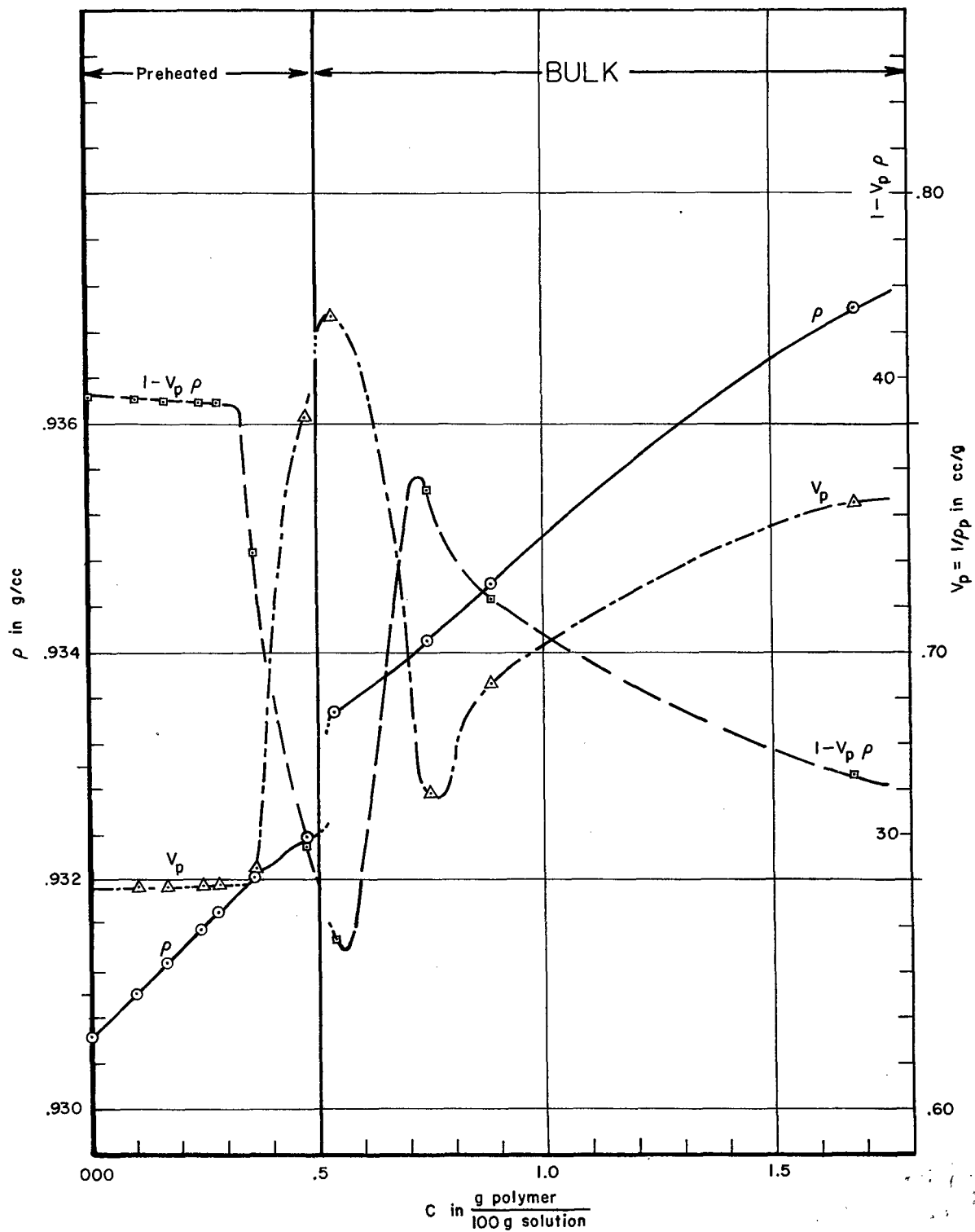


Figure 9. Pycnometry of PBI in DMAC at 30°C

The following viscosity measurements of PBI in DMAC were carried out with an Oswald-Fenske Viscometer: (a) Bulk polymer at 25°C; (b) Bulk polymer at 30°C; (c) Preheated batch at 30°C. The following functions were calculated and plotted for each case: η_{sp} vs $c = \text{g polymer}/100 \text{ g solution}$, η_{sp}/c vs c , and η_{sp}/ϕ vs $\phi = \text{cc polymer}/100 \text{ cc solution}$ (See Figures 10,11,12,13). From the expanded plot of voluminar reduced viscosity (Figure 13) the voluminar intrinsic viscosity was determined:

$$[\eta]\phi = 90.6.$$

Similar to the findings in determining densities above, the viscosity measurements at 30°C exhibit an abnormal behavior with a transition beginning at approximately $c = 0.3\%$.

The preliminary sedimentation experiments were performed at different speeds. Finally, the speed 50, 740 RPM was established. Two standard aluminum cells, 12 mm and 30 mm thick, were utilized in conjunction with the Schlieren Optics of the instrument. The results are given in Figure 14. The average extrapolated value for sedimentation constant was determined as: $s_0 = 1.776 \text{ sved.}$

Measurements of diffusion and polydispersity will be continued when fabrication of a new synthetic boundary cell is completed. Utilizing the data from the sedimentation and velocity measurements one can show that the molecular weight of the sample under investigation cannot exceed 20,400.

2. Viscosity and Osmometry of Whole and Fractionated Polymer Solutions

The intrinsic viscosity, $[\eta]$, of a sample of PBI prepared by Celanese Corp. has been determined in several solvents; dimethylformamide (DMF), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO) and N-methylpyrrolidone (NMP). The measurements were made at 30°C using a Cannon-Ubbelohde dilution viscometer No. 75. The values obtained are given as follows, where $[\eta]$ is given in dl/gm: DMAC - 0.64, 0.65, 0.67, 0.69 (four different determinations); DMF - 0.63, 0.53 (two determinations); and DMSO - 0.71; NMP - 0.65. These data are not as reliable nor consistent as one would expect from simple intrinsic viscosity measurements. The apparent reason for these variations arises from the difficulty in determining concentration values. It has been normal practice to evaporate a solution of known volume or weight to dryness and thereby calculate the concentration of the solution. However, in the case of PBI in all of the solvents mentioned above, it has been most difficult to bring the solid determinations to constant weights even after drying for up to six weeks and to temperatures of 200°C. To date, no clear cut solution to this problem has been found; however, several approaches are being investigated.

In the course of dissolving PBI in various solvents, it was observed that a marked difference existed in the rates of solution. In fact, certain solvents (DMF and DMAC) which were reported to dissolve the polymer completely, exhibited peculiar solvation of the polymer in so far as the rate of solution was unusually dependent on factors of agitation and heating. In addition, a certain portion of the polymer would dissolve only after a long duration of heating and stirring. It was assumed that this behavior might be attributable to a pronounced solubility dependence on molecular weight.

Accordingly, an attempt was made to determine whether or not molecular separation based on molecular weight was possible by extraction. A sample of PBI was extracted with DMF for about 50 hours in a Soxhlet apparatus. Approximately thirty percent of the polymer dissolved

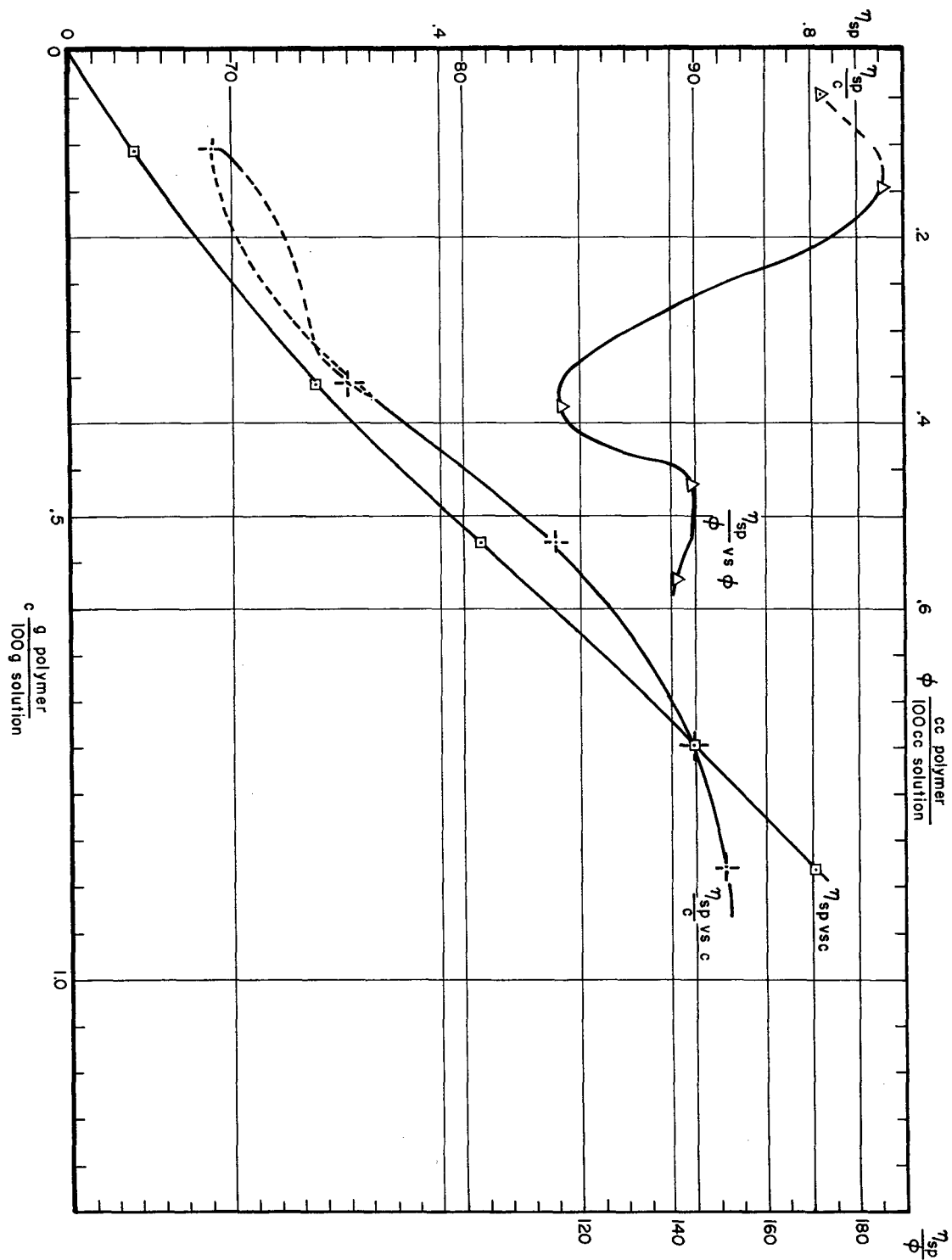


Figure 10. Viscosity of Bulk PBI in DMAC at 25°C

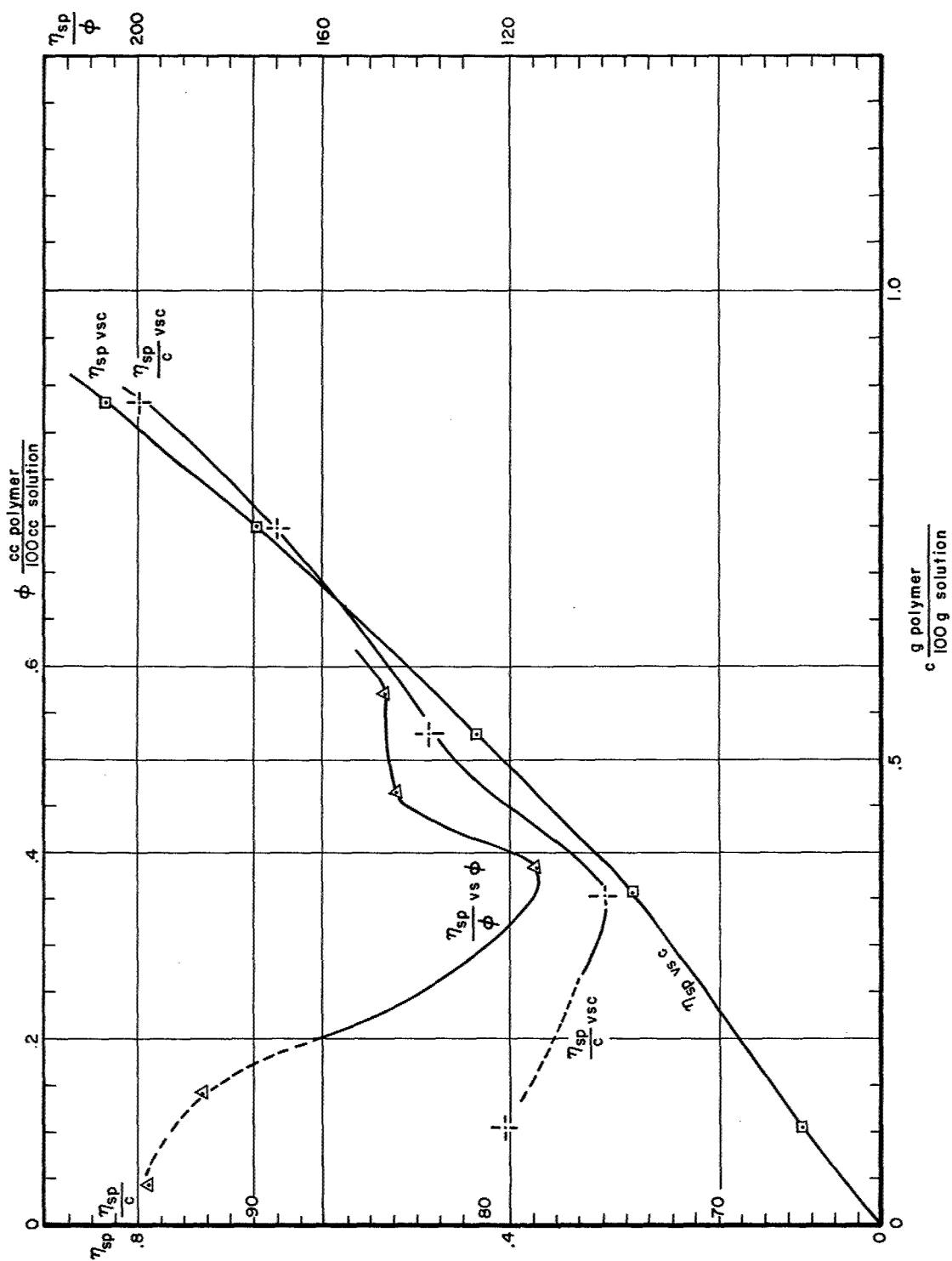


Figure 11. Viscosity of Bulk PBI in DMAC at 30°C

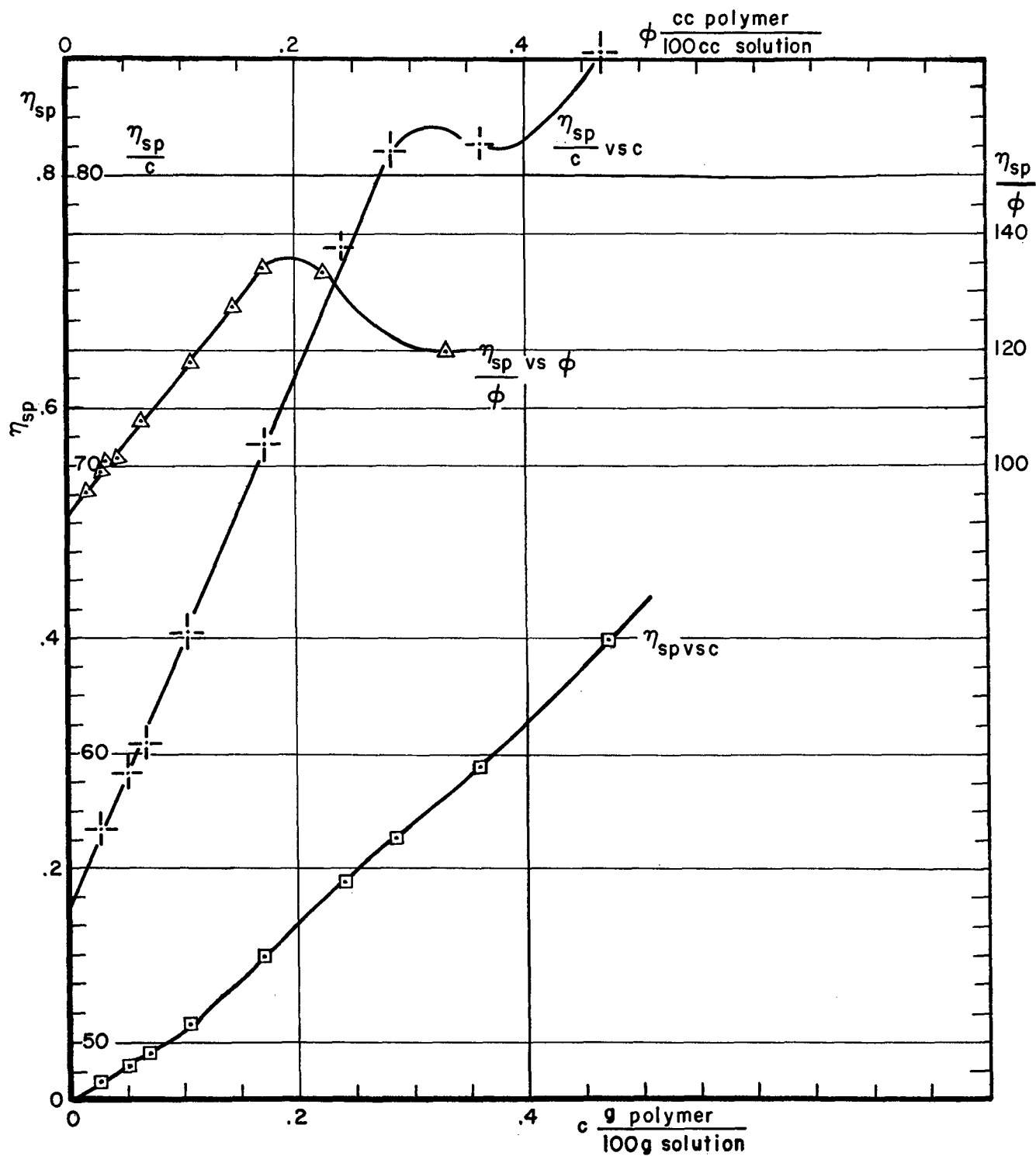


Figure 12. Viscosity of Preheated PBI in DMAC at 30°C

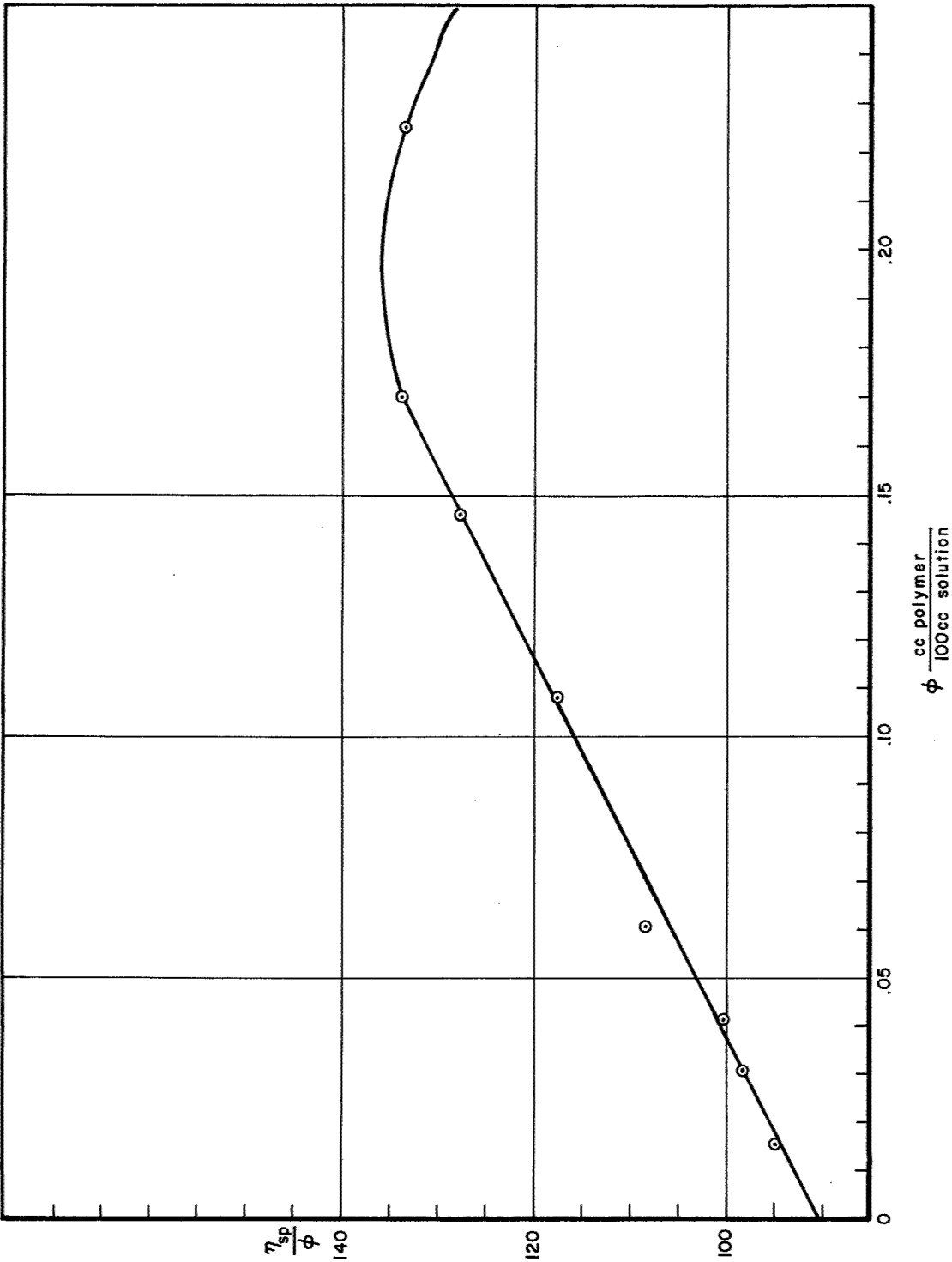


Figure 13. Voluminar Reduced Viscosity of Preheated PBI in DMAC at 30°C

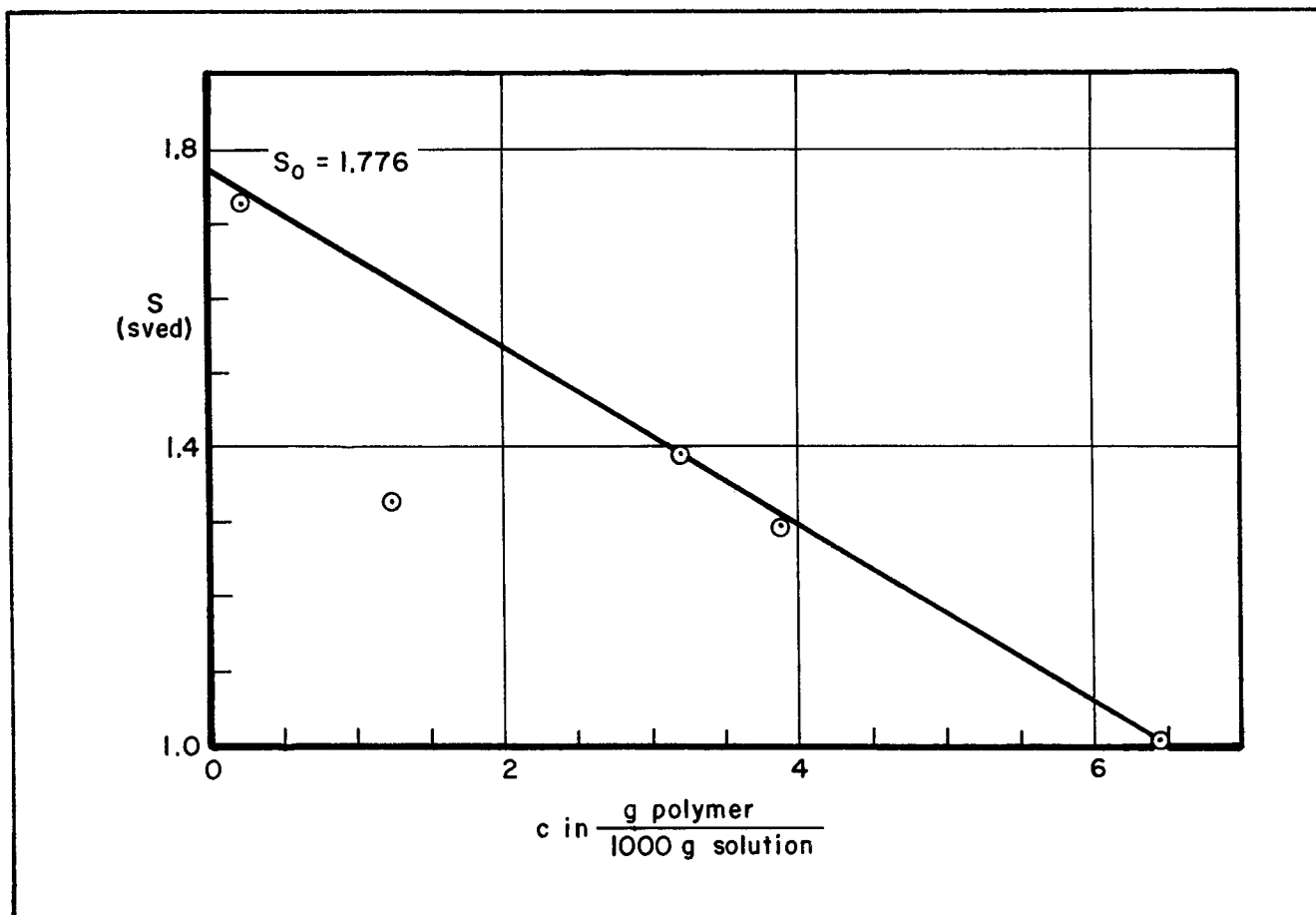


Figure 14. Sedimentation of PBI in DMAC at 30°C

during this time. Both the residue and extract were recovered, dried, and subsequently dissolved in DMAC for intrinsic viscosity measurements. The residue had a value, $[\eta] = 0.86$ dl/gm, the extract a value, $[\eta] = 0.48$ dl/gm, whereas the bulk polymer had a value $[\eta] = 0.66 \pm 0.03$ dl/gm. Even taking into consideration the unreliability of a given intrinsic viscosity determination, it appears that molecular weight separation has been accomplished.

Encouraged by these results a systematic extraction of a larger sample of PBI has been carried out with a variation of temperature in the extraction cup and a subsequent change from DMF as the extraction solvent to DMAC. In this manner, five 'fractions' of PBI have been obtained and will be studied to determine if a fine fractionation of PBI can be accomplished by an extraction technique.

Osmotic pressure measurements were also made. A portion of the DMF-extraction residue was dissolved in DMAC and examined in a Mechrolab high-speed membrane osmometer at 37°C. Because this sample exhibited some diffusion, the data was obtained as a function of time and back extrapolated to zero diffusion. By this technique, osmotic pressure values (π) were obtained and a plot of π/c vs c (where c is concentration in gm/cm^3) was made. The extrapolation to zero concentration yielded a number-average molecular weight of $1.73 \times 10^4 \pm 0.02$ and the slope gave a value of $2.5 \times 10^{-3} \pm 0.5 [\text{mole gm}^{-2} \text{cm}^3]$.

Although diffusion occurred, it appears that the molecular weight determination is quite acceptable. Nevertheless, if molecular weight separation was truly affected by extraction, then the extraction residue sample studied does not accurately represent the number-average molecular weight of the whole polymer. One would naturally assume on the basis of the viscosity data presented previously that the number-average of the whole polymer may be considerably lower than the value determined. This being the case, diffusion may be an insurmountable problem in determining the number-average molecular weight of the whole polymer by normal membrane osmometry.

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